

Density Functional Theory Calculations for Simple Oxametallacycles: Trends across the Periodic Table

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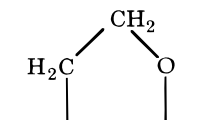
Density functional theory (DFT) was used to calculate the structures of simple oxametallacycles, generated by inserting one or two metal atoms in the C–O bond of the ethylene oxide molecule, for 14 different transition metals (groups VIIIa–c, Ib, IIb). The calculated energetic stability of these complexes generally decreases from left to right of the periodic table and from top to bottom of each group of metals. Silver, which is unique among these metals in catalyzing selective ethylene epoxidation, gives an oxametallacycle intermediate that is more stable than ethylene oxide by ca. 10 kcal/mol. The modest stability of this intermediate may explain the formation of the less energetically favorable C₂H₄O isomer, ethylene oxide, on silver catalysts. The calculated relative stabilities of oxametallacycles versus acetaldehyde on various metal surfaces are consistent with previous experimental observations that an oxametallacycle is the preferred intermediate in ethanol decarbonylation on the Rh(111) surface, whereas η^2 -CH₃CHO is preferred on the Pd(111) surface.

1. Introduction

Ethylene oxide is among the most important chemical products made by selective hydrocarbon oxidation.^{1–4} Its importance stems from the fact that it is a small molecule containing two carbon atoms and an oxygen atom, all bonded to each other via single bonds, in a relatively high-strain three-member ring configuration. This particular structure allows easy addition of other organic functions to the epoxide unit, and hence ethylene oxide serves as a useful chemical intermediate from which other important chemicals (e.g., ethylene glycol) can be derived. For more than a half century, silver has remained the unique catalyst for ethylene epoxidation. Although mechanistic understanding of the partial oxidation of ethylene to ethylene epoxide has been the target of numerous studies in surface science and catalysis,^{5–9} several fundamental questions remain with no satisfactory answer. It is only within the past 15 years that convincing evidence regarding the nature of the active oxygen species on the silver catalyst surface was offered; chemisorbed atomic oxygen (not dioxygen) is responsible for epoxidation.¹⁰ The oxygen atoms that attack the olefin double bond are typically described as electrophilic, and the charge on these species continues to be debated,^{11–13} as the form of atomic oxygen most accessible in surface science studies is clearly nucleophilic.¹¹ In addition, the roles of chlorine and alkali promoters are still incompletely defined, as are the identity of organic intermediates and the sequence of elementary reaction steps leading from reactants to products.^{12–13} Indeed, it is remarkable that so much attention has been focused on surface oxygen species and so little on other adsorbates in this reaction. It is also unclear why silver is unique in its activity and selectivity for ethylene epoxidation. The primary motivation of this work is to attempt to address the unique epoxidation activity of silver, through a comparative study between different

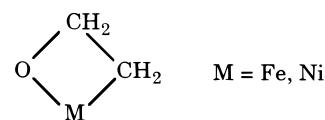
transition metals that could in principle serve as oxidation catalysts. This question is especially timely, given the recent commercialization of a new process for epoxidizing butadiene with a silver catalyst.¹⁴

This report focuses on surface oxametallacycle complexes. These complexes, typically depicted on surfaces by structures such as



have been invoked as intermediates in oxygenate surface reactions on Rh, Pd, and Ag by several groups,^{11,15–30} and have been implicated in the formation of epoxides on silver surfaces.^{11,20,21} We have recently interpreted the chemistry of iodoethanol (ICH₂CH₂OH) on Ag(110) in terms of an oxametallacycle intermediate stable above 300 K.³¹ However, there is at this point no published spectroscopic confirmation of the existence of an oxametallacycle in any of the examples for which surface oxametallacycles have been proposed.

In homogeneous catalysis, oxametallacycles (also referred to as metallaoxetanes) have been proposed as intermediates in an even wider variety of reactions, including epoxidation and asymmetric dihydroxylation of olefins.^{32–37} Although these intermediates are also somewhat elusive,³² spectroscopic and/or crystallographic evidence does exist for several stable metallaoxetane complexes. Metallaoxetanes containing iron and nickel atoms, for example



have been identified in matrix isolation experiments by Margrave and co-workers.^{38,39} These examples of metallaoxetane

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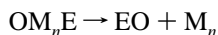
identification from organometallic chemistry all involve a single metal atom, and thus the metallaoxetanes are four-membered rings. On metal surfaces, coordination to multiple surface atoms is quite probable as pointed out previously,²⁶ and larger cyclic structures incorporating more than one metal atom may be more stable, as they would be less strained. A previous extended Huckel theory calculation by Calhorda and Friend⁴⁰ supports this suggestion, and the present work also explores the relative stabilities of oxametallacycles incorporating one metal atom (which we designate as OMEs) and two metal atoms (designated as OMMEs).

Among the major reaction channels proposed for the decomposition of metallaoxetanes in homogeneous catalysis,³² the following three appear to be most relevant to reactions on transition-metal surfaces: (i) alkene elimination with simultaneous release of a metal–oxygen complex, (ii) carbonyl elimination with a methylene (CH₂) bonded to the metal, and (iii) epoxide elimination accompanied by the release of a free metal center. In the present work, the elementary reaction step of oxametallacycle decomposition to ethylene oxide and a free metal center is isolated from the overall reaction pathway and studied in detail for different transition metals that are neighbors to Ag in the periodic table and could in principle serve as alternative epoxidation catalysts. We recognize that different products are likely to be favored on different metals and that the formation of oxametallacycle intermediates may not be feasible on some of the metals studied. Nevertheless, examination of the relative energetic stabilities of oxametallacycle intermediates for an array of metals offers substantial insight for (i) understanding differences between neighboring metals as far as the ethylene epoxidation catalysis is concerned and (ii) potentially explaining the uniqueness of silver for ethylene epoxidation. Furthermore, comparison of the stability of the oxametallacycle intermediate with that of its aldehyde isomer may explain experimental observations regarding preferred alcohol reaction pathways on different metal surfaces.

2. Method of Calculation

The Amsterdam density functional (ADF)^{41–43} program was used to perform full geometry optimizations and calculate total energies and relative energetic stabilities of the oxametallacycle complexes selected for this study. ADF represents the molecular orbitals as linear combinations of atomic Slater-type orbitals. The Kohn–Sham one-electron equations are solved using Vosko–Wilk–Nusair (VWN) functional⁴⁴ to obtain the local potential. Gradient corrections for the exchange (Becke functional)^{45,46} and correlation (Perdew functional)⁴⁷ energy terms were included self-consistently. All the results presented here are based on spin-unrestricted frozen-core calculations; in particular, for the carbon and oxygen atoms, a frozen core potential is used for the 1s electrons, whereas the frozen core extends to different electrons for the metal atoms used (Ag-3d, Au-5p, Cd-3d, Co-2p, Cu-2p, Fe-2p, Ir-5p, Ni-2p, Os-5p, Pd-3d, Pt-5p, Rh-3d, Ru-3d, and Zn-2p). No relativistic effects have been included in modeling the core electrons. The basis sets implemented are of double- ζ quality, except for the 3d orbitals of the first-row transition metals which were represented by triple- ζ basis sets.

Reaction energies were calculated for the oxametallacycle (OM_nE) decomposition to ethylene oxide (EO) plus bare metal center (M_n),



according to the expression

$$\Delta H_{\text{rxn}} \approx \Delta E_{\text{rxn}} = E(\text{OM}_n\text{E}) - \{E(\text{EO}) + E(\text{M}_n)\} \quad (1)$$

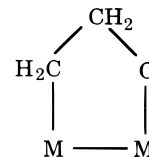
where $E(\text{EO})$ and $E(\text{M}_n)$ are the respective total energies of free ethylene oxide and the bare metal cluster consisting of n atoms of metal M. $E(\text{OM}_n\text{E})$ is the total energy of the oxametallacycle complex, which is created by the insertion of the bare metal cluster (M_n) into the C–O bond of the EO molecule. Exploratory calculations performed on oxametallacycles involving a metal dimer, for several of the 14 transition metals studied, suggest that the relative stabilities of these complexes remain by and large unaffected by whether the metal–metal bond length was fixed or allowed to relax in the course of energy minimization. However, all total energies calculated for ethylene oxide, bare metal clusters, and oxametallacycle complexes, as reported here, correspond to fully relaxed geometries (including the metal–metal bond), unless otherwise stated.

A negative ΔH_{rxn} value corresponds to an oxametallacycle that is energetically stable with respect to metal elimination to produce an EO molecule and a bare metal cluster at infinite separation. Identifying the ground-state of transition-metal complexes often involves calculating the total energy of several alternative electronic configurations, with different numbers of unpaired electrons. All the results given in the next section correspond to the ground-state configurations of both the bare metal cluster and the oxametallacycle bonded to the metal cluster.

3. Results and Discussion

We begin with a brief discussion of calculations on the stability of oxametallacycle complexes generated by inserting a single metal atom in one of the two C–O bonds of the ethylene oxide (EO) molecule. The four-member ring structures (OMEs) were calculated to be more stable than an EO molecule and a single metal atom at infinite separation, for all but two metals studied: Ag and Cd. The Ag₁-oxametallacycle is less stable than an isolated silver atom and EO molecule by ca. 19 kcal/mol, whereas the Cd₁-oxametallacycle is less stable by ca. 5 kcal/mol with respect to the corresponding products. As a consequence, Ag and Cd four-member OMEs are unlikely to be formed, because of energetic limitations. Gold- and zinc-oxametallacycles are slightly stable, with the corresponding, elimination reaction being almost thermoneutral (ca. 0 and 4 kcal/mol, respectively). Metal elimination to form ethylene oxide from the four-member OMEs for the rest of the transition metals studied is endothermic by between ca. 90 and 18 kcal/mol, depending on the metal.

Although calculations for four-member ring OMEs provide a basic understanding of relative trends for transition-metal oxametallacycles, calculations on the stability of five-member ring oxametallacycles (OMMEs) generated by the insertion of a metal dimer into one of the two C–O bonds of the EO molecule are expected to offer a better model for the oxametallacycles likely to be formed on extended catalytic surfaces. Such structures may be depicted schematically as



and a representative fully optimized structure for the Ag₂-

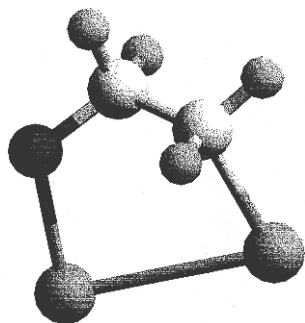
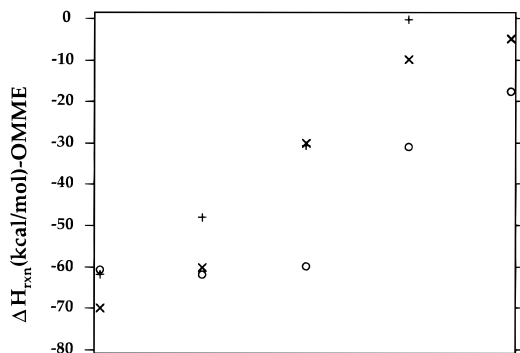


Figure 1. Fully optimized Ag_2 -oxametallacycle structure. Bond lengths are: $r(\text{Ag}-\text{Ag}) = 3.002 \text{ \AA}$, $r(\text{Ag}-\text{O}) = 2.155 \text{ \AA}$, $r(\text{O}-\text{C}) = 1.41 \text{ \AA}$, $r(\text{C}-\text{C}) = 1.516 \text{ \AA}$, $r(\text{Ag}-\text{C}) = 2.255 \text{ \AA}$.



○	Fe	Co	Ni	Cu	Zn
×	Ru	Rh	Pd	Ag	Cd
+	Os	Ir	Pt	Au	
	Period VIIIA	VIIIB	VIIC	IB	IIB

Figure 2. Calculated relative stability of five-member ring oxametallacycles (OMMEs) for 14 transition metals. The more negative ΔH_{rxn} , the more stable the corresponding OMME is with respect to formation of ethylene oxide (EO) and a metal dimer ($\text{M}-\text{M}$) at infinite separation.

oxametallacycle is shown in Figure 1. Extended surfaces provide a large number of neighboring metal atoms which could be incorporated in cyclic intermediates such as oxametallacycles. Moreover, five-member ring structures are in general more stable than four-member ring structures, primarily because of the reduced strain energy of the five-member ring configuration. This expectation is confirmed by the results of our calculations for OMMEs; in contrast to the results obtained for OMEs, where the Ag and Cd structures were unstable, the OMMEs were found to be stable relative to EO and the metal dimer at infinite separation between each other, for all 14 metals studied.

Figure 2 illustrates the endothermicity of the OMME decomposition reaction into EO and the corresponding metal dimer ($\text{M}-\text{M}$). The Au_2 -oxametallacycle is the least stable oxametallacycle (nearly thermoneutral decomposition reaction), whereas the OMME decomposition reaction for the rest of the metals studied is endothermic by ca. 70–5 kcal/mol, depending on the metal. In particular, the decomposition of the Ag_2 -oxametallacycle into $\text{EO} + \text{M}-\text{M}$ requires ca. 10 kcal/mol, suggesting that, if an oxametallacycle were formed on a silver surface, it would be moderately stable. The moderate stability of a possible catalytic reaction intermediate is in accord with Sabatier's principle⁴⁸ and provides some indication about possible reasons for the uniqueness of silver as an ethylene epoxidation catalyst.

The results in Figure 2 show the existence of a general trend characterizing the stability of OMME intermediates: the endothermicity of their decomposition reaction decreases from left to right of each row of metals. Similarly, the endothermicity

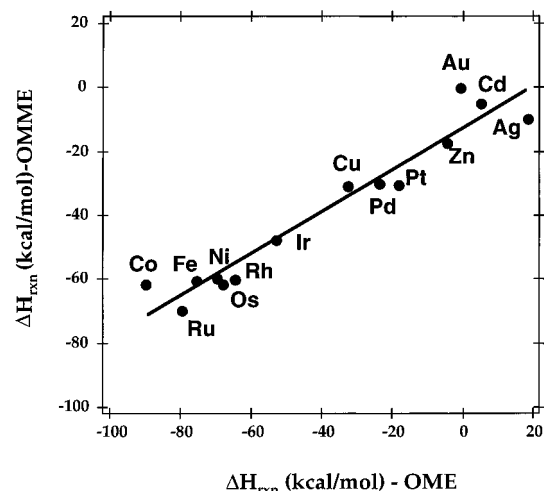


Figure 3. Parity plot for comparing calculated relative stability of five-member ring oxametallacycles (OMMEs) versus calculated relative stability of four-member ring oxametallacycles (OMEs) for 14 transition metals. The straight line drawn (slope = 0.7) is the best linear fit through the data points. If both cluster models predicted the same stabilities, all data points would lie on the diagonal of the plot.

generally decreases with increasing atomic number within each column of the periodic table of transition metals. The latter trend in relative OMME stability within a group of metals seems to be violated for the Fe group, but it should be noted that the range of values for the heat of reaction is rather small for the OMMEs of this particular group. Although total energies calculated for oxametallacycles involving third-row metals are less reliable due to neglect of relativistic effects in the present calculations,⁴⁹ the results for oxametallacycles of the second-row metals, including silver, are expected to be reliable, since relativistic effects are less important for second-row elements in general. The validity of these results for oxametallacycles of second-row metals is further supported by the excellent quantitative agreement found between the experimental HREELS spectrum of a silver-oxametallacycle and the theoretical infrared spectrum derived from frequency calculations⁵⁰ of the fully optimized Ag_2 -oxametallacycle structure shown in Figure 1.

The effect of the number of metal atoms inserted in the C–O bond of the EO molecule is examined in Figure 3, where the relative energetic stability of five-member ring OMMEs is plotted against the relative energetic stability of four-member ring OMEs. If the stability of the oxametallacycle intermediate were independent of the number of metal atoms involved in the ring structure of the intermediate, all 14 points shown would lie on the diagonal line (slope = 1). Our results indicate that, even though there is some dependence of the energetic stability on the number of metal atoms involved, there still exists a linear correlation between the stability of OMMEs and the stability of OMEs. (The slope of the best-fit line through the points, 0.7, as shown in Figure 3, is less than unity.)

Further exploratory calculations, performed for a subset of the above 14 metals, on oxametallacycles spanning two metal atoms of a three or four metal atom cluster suggest that the heat of the oxametallacycle decomposition depends slightly on the number of metal atoms in the cluster, but the previously outlined relative trends remain practically unchanged. To further examine the cluster size effect on the relative stability of oxametallacycles, we have extended our studies to larger metal clusters for silver and copper. As shown in Table 1, the absolute magnitude of the heat of oxametallacycle decomposition varies only by ca. 2 kcal/mol in changing the coordination of the copper dimer to which the organic ring is bonded, from 0 to 10

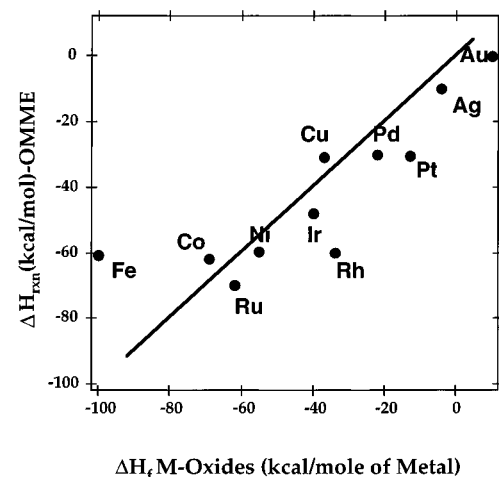
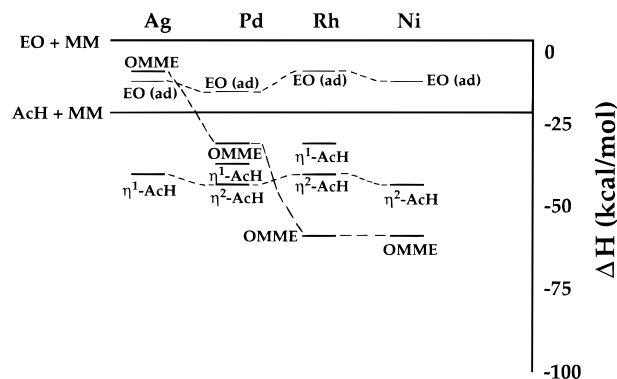
TABLE 1: Calculated Heat of Oxametallacycle Decomposition (ΔH_{rxn}) on Silver and Copper Clusters of Different Sizes^a

cluster size (metal atoms)	ΔH_{rxn} (kcal/mol)	
	Ag	Cu
2	-9.95	-30.80
8	-10.96	
12	-14.60	-32.45
15	-13.82	

^a A metal dimer is always inserted to the C–O bond of EO molecule, but the number of metal atoms surrounding this dimer changes from cluster to cluster. All the clusters represent a local truncation of the (110) surface of the corresponding metals. Values given for ΔH_{rxn} correspond to structures resulting from the optimization of the organic part of the oxametallacycle only, whereas metal–metal bond lengths were kept fixed at their bulk lattice constant values, for the calculation of the total energies of both the oxametallacycle intermediate and the bare cluster.

additional metal atoms surrounding the dimer, in a configuration simulating a local truncation of the (110) surface. The observed variation is certainly within the accuracy limits of DFT methods, and one can safely conclude that there is no important cluster size effect on the calculated oxametallacycle stability, at least for the case of copper. The heat of silver-oxametallacycle decomposition fluctuates with the number of atoms used in the clusters (in configurations simulating the Ag(110) surface) more than in the case of copper. However, even though the ratio of this fluctuation to the heat of decomposition is considerable, the absolute magnitude of the change (ca. 4 kcal/mol) is comparable with the accuracy limits of DFT methods. These results indicate that although cluster size can have an important effect on the binding energy of various atoms and molecules on several transition metals,^{51,52} it does not play a key role in determining the relative stability of oxametallacycles. The weak sensitivity of the calculated heat of oxametallacycle decomposition to cluster size suggests that the local coordination of the oxametallacycle intermediate is not particularly important, in accord with experimental observations suggesting that ethylene epoxidation on silver catalysts is structure-insensitive, with turnover rates independent of silver cluster size.⁹ The limited cluster size effect demonstrated by our calculations implies that comparative studies of the stability of oxametallacycle intermediates need not necessarily involve extensive calculations with large metal clusters.

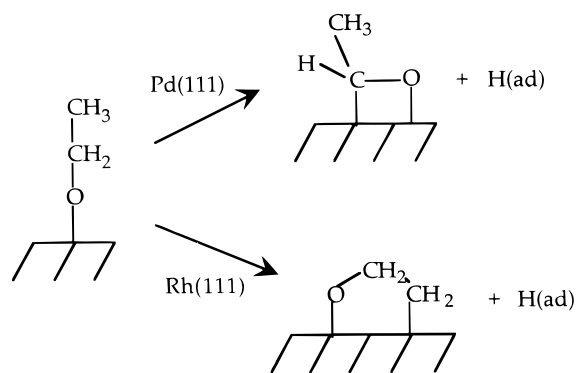
The decomposition reaction of OMMEs to EO and a metal dimer involves breaking two bonds (M–C and M–O) and forming a new C–O bond. Therefore, differences in the heats of reaction between OMMEs of different metals should reflect differences in the strengths of the bonds being broken during the decomposition process. Since most bonds to metal atoms typically follow the same trends across the periodic table, there is a strong correlation between the heats of adsorption on metals and the heats of formation of the corresponding oxides.⁵³ Figure 4 demonstrates a linear correlation between the heat of OMME decomposition, as calculated in this work, and the heat of formation of the corresponding metal oxides, as available in the literature.⁵⁴ Although there is some scatter of the data points around the diagonal, it is clear that the relative energetic stability of simple oxametallacycles follows the trends describing the M–O bond strength; the stronger the M–O bond, the more stable is the OMME intermediate. The periodic trends in surface metal–oxygen bond strength can be understood from general principles of surface bonding.^{48,55} Bonds to transition-metal surfaces result from mixing metal orbitals with adsorbate orbitals in bonding and antibonding combinations. The important

**Figure 4.** Parity plot for comparing calculated stability of five-member ring oxametallacycles (OMMEs) versus heat of formation of the corresponding metal oxide for 14 transition metals. The diagonal line of the plot is drawn as a guide to the eye.**Figure 5.** Calculated relative stability of five-member ring oxametallacycles (denoted by OMME) and experimental heats of adsorption for ethylene oxide (EO) and two forms of adsorbed acetaldehyde (η^1 -AcH and η^2 -AcH) for four transition metals.

difference from one transition-metal to the next is in the position of the d-band relative to the Fermi level or, equivalently, the d-band occupancy. Metals with more d-electrons will have higher occupations of the antibonding orbitals, and the metal–adsorbate bonds will become weaker.

The calculated relative stability of OMMEs for a selected set of metals (Ag, Pd, Rh, Ni) is sketched in Figure 5, along with experimental data^{22,57–65} for the heats of adsorption of EO and its isomers η^1 - and η^2 -CH₃CHO on the same metals. This figure was constructed as follows. The calculated energy of a free EO molecule plus the metal dimer at infinite separation was taken as the zero of energy for each metal. The calculated ΔH_{rxn} values from eq 1 give the energy of the OMMEs relative to this energy zero in each case. Free acetaldehyde was calculated (using ADF) to be favored energetically over EO by 24 kcal/mol, in agreement with tabulated heats of formation for these isomers.⁵⁶ Thus, the possible oxametallacycle decomposition products, acetaldehyde plus metal dimer, lie 24 kcal/mol below EO plus metal dimer, indicated by the horizontal line in Figure 5. In principle, one can also calculate heats of adsorption of EO or acetaldehyde on metal clusters or surfaces. In fact, both experiments^{22,57–65} and theory^{65,66} have shown molecular adsorption of these compounds to be weak and fairly insensitive (to within a few kcal/mol) to the identity of the metal. Typical heats of molecular adsorption on transition-metal surfaces are 10–15 kcal/mol for EO and 15–20 kcal/mol for

SCHEME 1



η^2 -acetaldehyde. Heats of adsorption from TPD experiments with EO and acetaldehyde (in η^1 -O and/or η^2 -CO configurations, as observed in each case) have been incorporated in Figure 5. The measured heats of adsorption represent the separation in Figure 5 between the values for adsorbed species and the calculated energy of the corresponding free molecule and metal dimer.

The calculated and measured energies in Figure 5 suggest that the stability of oxametallacycles relative to adsorbed EO and acetaldehyde depends strongly on the identity of the metal, as one might expect. These variations in energetic stability can explain several experimental observations regarding the selectivity of C_2 oxygenate reactions on transition-metal surfaces. For example, according to our calculations, the oxametallacycle intermediate (OMME) is more stable than either form of acetaldehyde on a Rh surface. We have previously shown that decomposition of ethoxide intermediates on Rh(111) does not proceed via an acetaldehyde intermediate, but instead appears to follow an oxametallacycle-mediated reaction pathway (Scheme 1).^{22–24} This observation is entirely consistent with the greater stability of the oxametallacycle on this metal. On the other hand, experiments with ethanol on a Pd(111) surface suggest that η^2 - CH_3CHO is the major intermediate product (Scheme 1),⁶⁰ in accord with the results of our calculations indicating that the Pd_2 -oxametallacycle is less stable than either form of acetaldehyde on Pd. Hence, the experimentally observed selectivity difference between alternative reaction pathways for alcohol chemistry on Pd and Rh surfaces can be explained based on simple thermodynamic arguments alone, since the pathway involving the most energetically stable isomer on each metal is preferred.

Another remarkable point demonstrated in Figure 5 is that the OMME and EO are energetically almost equally stable on a Ag surface. Therefore, the interconversion between these two isomers is nearly thermoneutral, suggesting that the synthesis of ethylene oxide from oxametallacycles is quite feasible on this metal. These calculations may also explain the absence of EO formation on other metals with more stable oxametallacycles; an OMME intermediate that is too stable would likely lead to the most energetically stable molecular product, acetaldehyde, since the corresponding activation barrier would be considerably smaller than the barrier leading to the least stable molecular product, EO. On the other hand, if the oxametallacycle were unstable on silver, it would likely not be formed at all. A moderately stable Ag-OMME, as predicted by our calculations, provides a feasible path for selective formation of the epoxide. Thus, silver's uniqueness as an ethylene epoxidation catalyst may be associated with its unique property of forming a moderately stable oxametallacycle intermediate. The rest of the metals studied form either too stable or marginally

stable oxametallacycle intermediates, rendering them less favorable as ethylene epoxidation catalysts.

4. Conclusions

Density functional theory methods provide an affordable and accurate tool for calculating the electronic structure and optimized geometry of systems including transition metals. Total energy calculations of individual molecular structures participating as reactants or products in various reaction steps lead to the derivation of accurate reaction energies and therefore to conclusions pertaining to the relative energetic stability of reactants and products.^{67–69} Following this approach, the relative stabilities of simple oxametallacycle complexes for the transition metals of groups VIIIa–c, Ib, and IIb have been investigated. In particular, we have found that the decomposition reaction of oxametallacycles toward ethylene oxide and the bare metal cluster becomes less endothermic as one moves to the right of each row of metals. Similarly, the endothermicity of the oxametallacycle decomposition reaction decreases with increasing atomic number within each group of metals. The above trends persist regardless of metal cluster size for two or more atoms, indicating that DFT can provide accurate information without necessarily resorting to computationally intensive large metal cluster calculations. The latter statement is most likely valid for structure-insensitive reaction steps, where the local coordination does not play a particularly important role.

The linear correlation found between the heats of formation of metal oxides and the calculated heats of the oxametallacycle decomposition reaction demonstrates the dominant role of the metal–oxygen bond in oxametallacycles in determining the stability of oxametallacycle intermediates. Oxametallacycles were calculated to be moderately stable (ca. 10 kcal/mol relative to free EO) on silver but were much more energetically stable for most of the other metals studied. This result may explain the formation of the less energetically favorable C_2H_4O isomer, ethylene oxide, on silver, since highly stable oxametallacycle intermediates would be expected to favor selectivity toward the most energetically preferred isomer. Furthermore, calculation of the relative stability of oxametallacycles provides substantial insight for explaining experimental observations for alcohol chemistry on various transition-metal surfaces, based on simple energetic arguments. In particular, our calculations predict that an oxametallacycle is energetically preferred on a Rh(111) surface, whereas η^2 - CH_3CHO is energetically preferred on a Pd(111) surface, in excellent agreement with existing experimental data.

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