

Stabilities of Substituted Oxametallacycle Intermediates: Implications for Regioselectivity of Epoxide Ring Opening and Olefin Epoxidation

J. Will Medlin, Manos Mavrikakis,[†] and Mark A. Barteau*

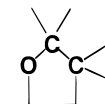
Center for Catalytic Science and Technology, Department of Chemical Engineering,
University of Delaware Newark, Delaware 19716

Received: August 10, 1999; In Final Form: October 19, 1999

Total energy density functional theory (DFT) calculations were performed to determine the relative stabilities of methyl substituted isomers of oxametallacycle intermediates potentially formed during ring-opening reactions of propylene oxide (PO) and isobutylene oxide (IO) on metal dimers. The relative stabilities of different oxametallacycle isomers may determine the regioselectivity of reactions involving these intermediates. In the ring opening of PO and IO, two oxametallacycle isomers may be formed: one in which the methyl groups are attached to the bridging carbon of the O–C–C backbone and one in which the methyl groups are attached to the surface-bound carbon. DFT calculations consistently indicate that oxametallacycles incorporating methyl groups attached to the bridging C atom are more stable by approximately 2–7 kcal/mol for all 14 metals studied. However, the relatively small thermodynamic stability differences between isomers suggest that kinetic barriers and the manipulation of these by surface modification may control the regioselectivity of reactions involving oxametallacycles in some cases. Computed oxametallacycle stabilities are compared with regioselectivities of epoxide ring opening and olefin oxidation reactions previously reported on metal surfaces and catalysts in order to examine which examples are consistent with the formation of the thermodynamically preferred oxametallacycle intermediate.

Introduction

Many surface science and theoretical studies of catalysis have focused on elucidating the mechanism of partial oxidation processes. Much attention, for example, has been devoted to understanding the mechanism of silver-catalyzed ethylene epoxidation.^{1,2} Understanding the reactivity of important intermediates is a key to developing mechanistic descriptions of such processes. One intermediate that has been proposed to be important in oxidation catalysis is the surface oxametallacycle:

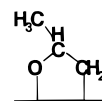


These species have been advanced as intermediates in numerous studies of oxygenate synthesis and decomposition,^{3–11} including those of epoxides. Recently, Jones et al. reported the first spectroscopic identification of a stable surface oxametallacycle synthesized from 2-iodoethanol on Ag(110).¹² The growing number of studies in which oxametallacycles (metallaioxetanes) are implicated suggests a need to understand their reactivity. Density functional theory (DFT) based predictions of the thermodynamics and kinetics of reactions involving oxametallacycles can be useful in defining the role of these intermediates in heterogeneous catalysis.

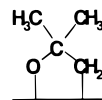
We have recently reported results of a DFT-based study of stability trends for C₂ oxametallacycles over a range of late-transition metals.¹³ These stability trends provided the first explanation for the differing reaction pathways observed for

alcohol decomposition on Pd(111) and Rh(111) and provided additional insights into the unique efficacy of silver as a selective olefin epoxidation catalyst. Although that study delineated stability trends for C₂ oxametallacycles, substituted oxametallacycles (in which substituent groups are attached to one of the two carbon atoms of the ring) were not considered. The primary focus of the present work is to evaluate stability trends for oxametallacycles in which pendant hydrocarbon ligands have been attached to the carbon atoms of the C₂ oxametallacycle.

Stability trends of substituted oxametallacycles have important implications for the regioselectivity of reactions involving oxygenates. To understand why, it is useful to examine chemistries proposed to involve oxametallacycle intermediates. For example, Xu and Friend have studied the oxidation of propylene to acetone on the Rh(111)-p(2 × 1)-O surface.⁹ This reaction was proposed to proceed through an oxametallacycle intermediate of the type



Xu and Friend have also studied the oxidation of isobutylene on Rh(111)-p(2 × 1)-O to form tertiary butanol.¹⁰ For this reaction, an oxametallacycle having the structure



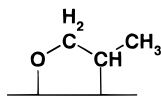
was proposed as a transient intermediate. Note that in both cases, the proposed oxametallacycle contains methyl groups bound to the bridging carbon of the O–C–C oxametallacycle backbone.

* To whom correspondence should be addressed.

[†] Present address: Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706.

One can envision isomers of these intermediates in which the methyl groups are attached to the surface-bound carbon of the oxametallacycle. For the oxidation of propylene and isobutylene on this surface, however, the formation of ketones and tertiary alcohols rather than aldehydes and primary alcohols was observed, suggesting that the linear isomers are not likely to be intermediates for these reactions.

In related work, Brown and Barteau studied the decomposition of propylene oxide on clean Rh(111).⁵ They proposed that this reaction proceeds through an oxametallacycle having the structure



Note that for this reaction, the proposed intermediate is an oxametallacycle with a methyl group attached to the surface-bound carbon rather than to the bridging carbon. This linear isomer was proposed on the basis of the similarity between the products of propylene oxide and 1-propanol decomposition and the dissimilarity between the products of propylene oxide and 2-propanol decomposition.^{4,7} Thus, the oxidation of propylene on oxygen-covered Rh(111) and the decarbonylation of propylene oxide on Rh(111) have been proposed to proceed through different oxametallacycle intermediates that are actually isomers of one another. Although oxygen can substantially modify surface reactivity¹⁴ and thus potentially change oxametallacycle stability, to date there has been no satisfactory explanation for the formation of different oxametallacycle isomers in these two reactions. Furthermore, there has been no detailed study of the extent to which the thermodynamic stability of one oxametallacycle isomer over the other may influence the reaction selectivity.

In studies of catalytic reactions proposed to proceed via oxametallacycle intermediates, Bartók et al. have studied the hydrogenolysis of propylene oxide over supported metal catalysts.^{15–17} They reported that propylene oxide reacts over reduced Pt, Pd, Cu, and Ni catalysts to form acetone and 2-propanol as major products. The formation of these products indicates ring opening via C–O bond cleavage at the unsubstituted end of the epoxide ring. That is, the reaction proceeds via an oxametallacycle intermediate in which a methyl group is bound to the bridging carbon, i.e., the branched isomer. However, Bartók et al. have also demonstrated that propylene oxide reacts on oxidized Cu and Ni catalysts to form primarily propionaldehyde and 1-propanol. These products indicate ring opening via C–O bond cleavage at the substituted end of the epoxide ring. Thus, an oxametallacycle with a methyl group bound to the surface-bound carbon (the linear isomer) could be a reaction intermediate. Again, it is unclear why different oxametallacycle isomers would be preferred for the reactions of propylene oxide on reduced and oxidized metal surfaces. A better understanding of the relative stabilities of oxametallacycle isomers is necessary to evaluate possible reasons for the observed selectivity patterns and to understand the regioselectivity of epoxide ring opening and olefin oxidation reactions.

We present here a series of DFT-based calculations to evaluate the stability of oxametallacycle intermediates of potential importance in these reactions. Thus, we have calculated the stability of each oxametallacycle isomer that could result from ring opening of propylene oxide and isobutylene oxide. These results are compared with those for ethylene oxide derived oxametallacycles and with experimental reports to determine

which of the above examples are consistent with the formation of thermodynamically preferred oxametallacycle intermediates.

Method of Calculation

The Amsterdam density functional (ADF)^{18–20} program was used for all total energy calculations, geometry optimizations, and vibrational frequency analysis in this study. ADF represents molecular orbitals as linear combinations of atomic Slater-type orbitals. Kohn–Sham one-electron equations are solved using the Vosko–Wilk–Nusair (VWN) functional²¹ to obtain the local potential. Gradient corrections for the exchange (Becke functional)²² and correlation (Perdew functional)²³ energy terms were included self-consistently. All results presented here are based on spin-unrestricted frozen-core calculations; specifically, 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. All frequency calculations were performed on fully optimized oxametallacycle structures using an integration accuracy of 10^{-6} .

Energies were calculated for oxametallacycle formation from the respective epoxide plus the bare metal center according to

$$\Delta H_{\text{rxn}} \approx \Delta E_{\text{rxn}} = E(\text{oxametallacycle}) - \{E(\text{epoxide}) + E(M_n)\} \quad (1)$$

where $E(\text{epoxide})$ and $E(M_n)$ are the respective total energies of the free epoxide and the bare metal cluster consisting of n atoms of metal M . Oxametallacycle complexes are created by insertion of the bare metal cluster (M_n) into a C–O bond of an epoxide. For convenience, we will refer to the oxametallacycle created by the insertion of a metal cluster into the ethylene oxide, propylene oxide, and isobutylene oxide molecules as OM_nE , OM_nP , and OM_nI , respectively. The insertion of the metal cluster into different ends of the propylene oxide and isobutylene oxide molecules creates two generic oxametallacycle structures. For these molecules, we refer to the oxametallacycle species formed from breaking the C–O bond at the substituted carbon as isomer **1** (the linear isomer for propylene oxide ring opening), and the species created by breaking the C–O bond at the unsubstituted carbon as isomer **2** (the branched isomer for propylene oxide ring opening).

A negative ΔH_{rxn} value corresponds to an oxametallacycle that is thermodynamically stable with respect to metal elimination to produce an epoxide 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 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.

Computational Results

In a previous study,¹³ we examined the stability of ethylene oxide derived oxametallacycles incorporating two metal atoms (referred to as OMMEs) across a range of late transition and noble metals. These OMME structures are formed (hypothetically) by the insertion of a metal dimer into a C–O bond of ethylene oxide. Calculations with metal dimers provide us with

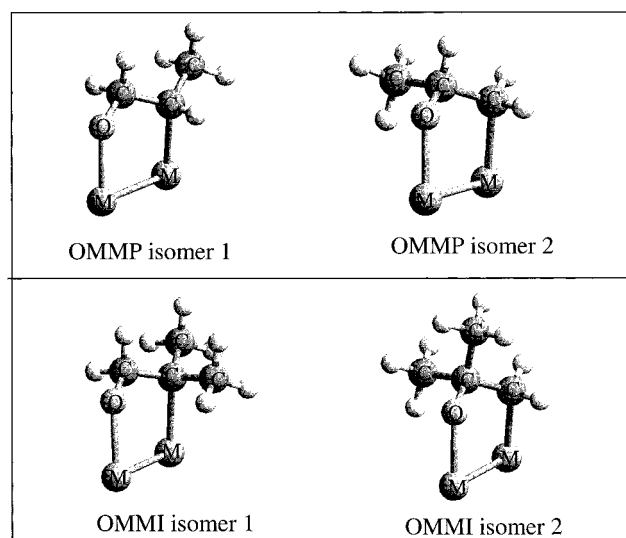


Figure 1. Structures of oxametallacycles examined in this work.

TABLE 1: Oxametallacycle Stability Values in kcal/mol^a

	OMME (ref 13)	OMMP isomer 1	OMMP isomer 2	OMMI isomer 1	OMMI isomer 2
Fe	-60.77	-55.23	-59.44	-52.09	-58.40
Ru	-70.02	-65.36	-68.94	-62.98	-68.12
Os	-61.85	-56.95	-60.13	-54.37	-59.16
Co	-61.90	-59.54	-63.78	-56.40	-62.48
Rh	-60.13	-56.05	-58.82	-54.39	-58.36
Ir	-48.06	-44.02	-46.41	-42.19	-45.71
Ni	-59.83	-54.50	-58.51	-51.24	-57.11
Pd	-39.10	-34.36	-38.56	-35.40	-38.37
Pt	-30.58	-27.76	-29.55	-27.05	-29.36
Cu	-30.80	-25.87	-30.12	-22.91	-27.11
Ag	-9.95	-4.92	-10.22	-2.19	-5.81
Au	-0.30	5.14	0.41	7.38	4.57
Zn	-17.49	-12.12	-16.12	-8.69	-15.44
Cd	-5.01	0.43	-2.60	3.49	-1.28

^a Stabilities of the more stable isomers for OMMPs and OMMIs are in boldface. ΔH_{rxn} values for oxametallacycle formation are obtained according to eq 1.

a computationally tractable means to determine relative stabilities of oxametallacycles on numerous metals with reasonable accuracy. Trends in relative stabilities of OMMEs were found to be largely independent of metal cluster size.¹³ In the present study, geometry optimizations were performed to determine the stability of five-membered-ring oxametallacycles created by the insertion of a metal dimer into a C–O bond of propylene oxide (PO) and isobutylene oxide (IO). Figure 1 shows the four structures examined. Geometries of both possible isomers of the propylene oxide oxametallacycle (OMMP) and isobutylene oxide oxametallacycle (OMMI) were optimized on all 14 metals selected. For each OMMP isomer, at least two stable oxametallacycle geometries were identified. The results here correspond to the most stable conformer for each isomer identified by these calculations.

Table 1 summarizes the relative stabilities of OMMP and OMMI oxametallacycles, including results from our previous investigation of the relative stabilities of ethylene oxide derived oxametallacycles (OMMEs) for the sake of comparison. These results indicate that the decomposition of oxametallacycles to form the bare metal dimer and corresponding gas-phase epoxide on gold and cadmium dimers is nearly thermoneutral. The reaction of oxametallacycles on other metals is endothermic; these oxametallacycles are more stable than the corresponding epoxide products by up to 70 kcal/mol. Note that olefin

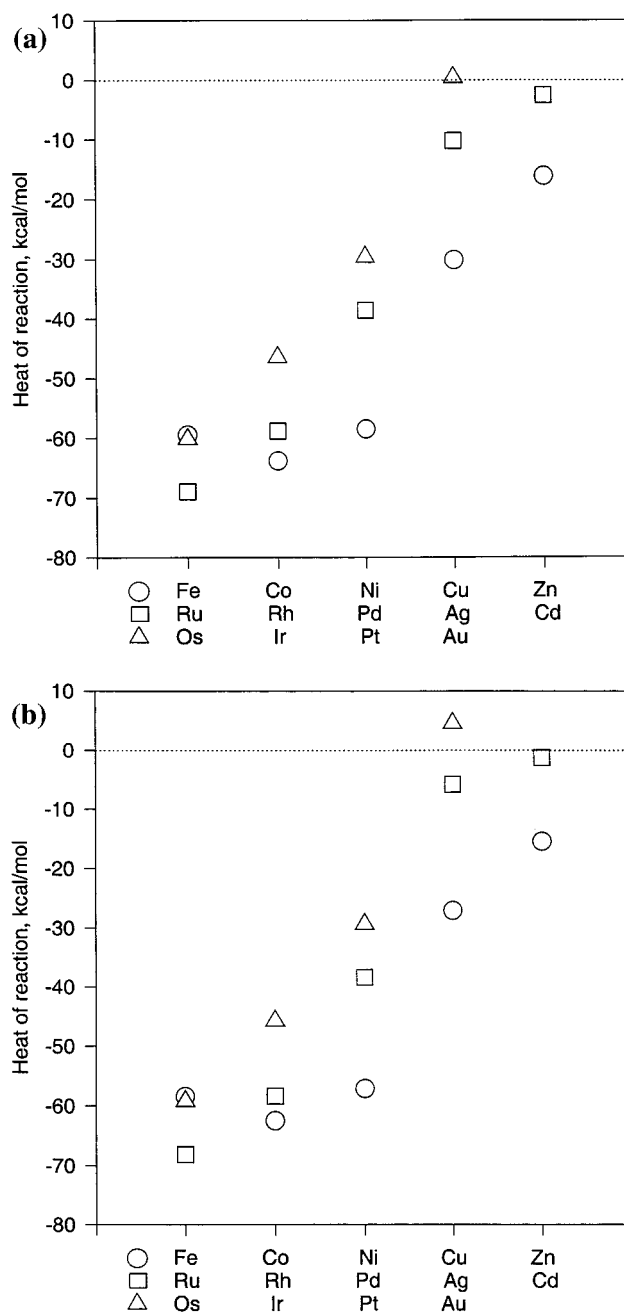


Figure 2. Stabilities for isomer 2 oxametallacycles across the periodic table: (a) OMMP and (b) OMMI.

epoxidations are exothermic by 25–27 kcal/mol;²⁴ thus, oxametallacycle formation from gas-phase olefins plus dioxygen would be an exothermic process on all of the metals examined. It is also important to recognize that OMMEs, OMMPs, and OMMIs are modestly stable (by 2–10 kcal/mol) on silver dimers with respect to epoxide elimination. The observation that the modest stability of oxametallacycles on metal dimers is a particular characteristic of silver provides a possible explanation for the uniqueness of silver as a selective epoxidation catalyst.¹³

Parts a and b of Figure 2 demonstrate the relative stabilities of OMMPs and OMMIs, respectively, as a function of position in the periodic table. For illustrative purposes, these energies are reported only for the isomer in which the methyl substituents are attached at the bridging carbon of the oxametallacycle (isomer 2). This isomer is the more stable for all metals studied. Figure 2 indicates that the stability of oxametallacycles generally decreases from left to right across the periodic table and from

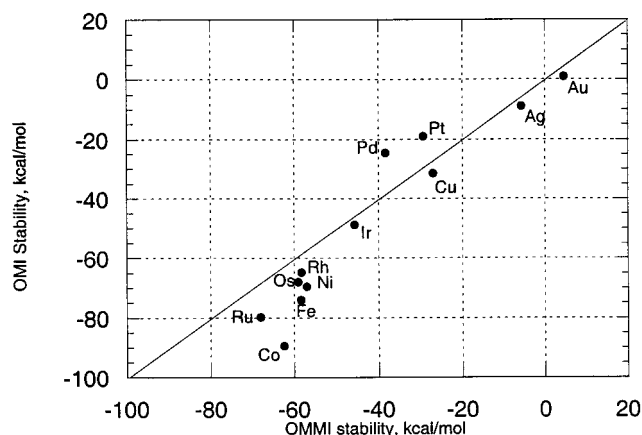


Figure 3. Parity plot of stability values for isomer 2 OMMIs versus OMIs (the diagonal line is included to guide the eye).

top to bottom of each column of metals. The same trends were observed in our previous calculations of OMME energies. Although there are a few exceptions to these general rules (specifically for the case of the Fe-group oxametallacycles), these exceptions are typically small in magnitude and may be related to the neglect of relativistic effects for f block transition metal complexes.²⁵

Although five-membered-ring oxametallacycles are in general expected to be more stable than four-membered-ring oxametallacycles because of lesser ring strain, one cannot exclude the possibility of exceptions to this rule. In cases where four- and five-membered rings have comparable stability values, examination of the vibrational modes of both structures in comparison with experimental vibrational data can provide conclusive evidence regarding the ring structure of the isolated oxametallacycle intermediate. For example, the oxametallacycle synthesized on Ag(110) from iodoethanol clearly corresponds to the five-membered-ring structure (OMME).¹² Figure 3 shows the results of comparing the relative stabilities of isomer 2 isobutylene oxide oxametallacycles characterized by a four-membered ring (OMI) and a five-membered ring (OMMI) for all 14 metals studied. Although there are some noticeable differences among oxametallacycle stabilities for certain metals, the relative stability of oxametallacycles on different metals is largely unaffected by the number of metal atoms inserted. This trend was observed for all oxametallacycles included in this study.

The effect of cluster size on the calculated relative stability of oxametallacycles is considered next. We have performed several geometry optimizations of oxametallacycles adsorbed on larger metal clusters, with special emphasis placed on 12-atom local truncations of the Ag(110) and Cu(110) surfaces. Cu and Ag were specifically selected for their catalytic relevance in reactions of epoxides and oxametallacycles,^{8,12,26} and the (110) facet was chosen because of our experimental verification of a stable OMME structure derived from 2-iodoethanol on Ag-(110).¹² Table 2 compares the effect of cluster size on the relative stabilities of OMMPs and OMMIs. Corresponding data derived for OMMEs¹³ have been included for comparison. In all cases, the organic part of the complex is directly bonded to only two atoms of the metal cluster used. Although the use of larger metal clusters has a small systematic stabilizing effect on oxametallacycles, this effect is generally less than a few kcal/mol, which is comparable to the accuracy of these calculations. Therefore, using metal dimers to obtain an understanding of the relative stabilities of oxametallacycles on different metals appears to be a reasonable approach with considerable computational simplicity.

TABLE 2: Effect of Cluster Size on Oxametallacycle Stability in kcal/mol^a

	Ag ₂	Ag ₁₂	Cu ₂	Cu ₁₂
OMME	-9.95	-14.60	-30.80	-32.45
OMMP, isomer 2	-10.22	-13.68	-30.12	-31.58
OMMP, isomer 2	-4.92	-8.34	-25.87	-26.09
OMMI, isomer 2	-5.81	-10.70	-27.11	-28.92
OMMI, isomer 1	-2.19	-5.19	-22.91	-22.62

^a Stabilities of the more stable isomers for OMMPs and OMMIs are in boldface.

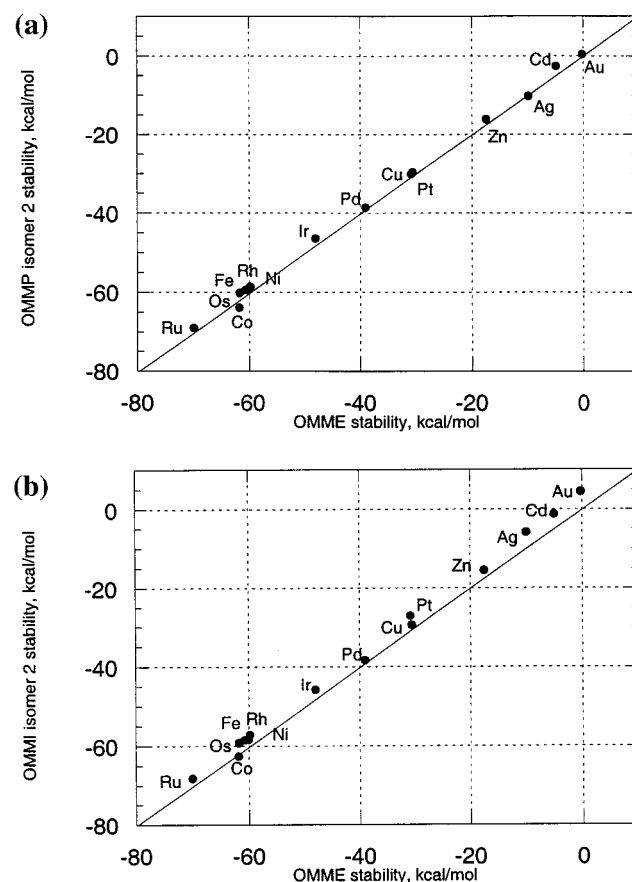


Figure 4. Parity plot of isomer 2 stability values from this work versus stability values for OMMEs from ref 13: (a) OMMP and (b) OMMI.

One of the most striking conclusions from our calculations is that the same stability trends are observed for all oxametallacycles that have been studied to date. Figure 4 demonstrates the excellent agreement of our results for the OMME, OMMP, and OMMI oxametallacycles, where only the stability of (the more stable) isomer 2 is shown for the OMMP and OMMI structures. Figure 4a indicates that there is a nearly linear relationship between the stabilities of OMMEs and OMMPs, and Figure 4b demonstrates a similar relationship between the stability of OMMEs and OMMIs. This strong agreement is an indication that the addition of methyl substituent groups does not have a significant effect on stability differences between oxametallacycles on different metals. Furthermore, these results, in connection with the linear correlation of oxametallacycle stabilities versus metal oxide heats of formation,²⁷ point to the dominant role played by the oxygen-metal bond strength in determining relative oxametallacycle stability. Most importantly, the comparable stabilities of OMMEs and these methyl substituted homologues, OMMPs and OMMIs, are consistent with the conclusion that barriers to selective propylene epoxidation lie elsewhere. The weak allylic C-H bonds of propylene lead

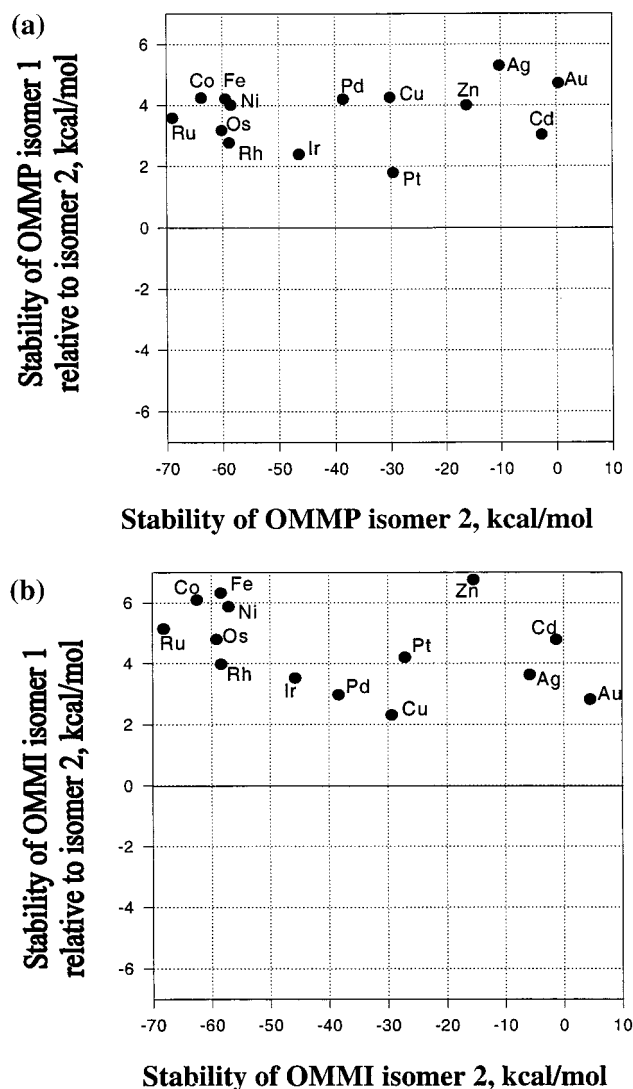


Figure 5. Stability of isomer 1 relative to isomer 2. Here, the relative stability is the stability difference between isomer 1 and isomer 2: (a) OMMP and (b) OMMI.

to more facile combustion of this molecule in parallel with epoxidation. The present calculations suggest that an oxametallacycle-mediated epoxidation pathway on silver could be as favorable for propylene as for ethylene if competing allylic combustion pathways for the former could be suppressed.

Having established that the trends in stability across the periodic table remain largely unaffected by the attachment of methyl substituent groups to OMMEs, we now turn our attention to the relative stability of the different oxametallacycle isomers studied in this work. Specifically, one of the principal goals of these calculations is to determine the identity and structure of the more stable OMMP and OMMI isomers. Identifying the more stable isomer may help to explain the regioselectivity of oxidation processes. In many cases, one would expect the more stable isomer to be preferentially formed along the reaction coordinate of these reactions. Parts a and b of Figure 5 show the relationship between the stabilities of each isomer for OMMP and OMMI oxametallacycles, respectively. In both cases, these figures show that isomer 1 is consistently less stable than isomer 2 for each metal dimer by 1–6 kcal/mol. Examination of the data in Table 1 reveals that the stability difference between the OMMI isomers is greater than between OMMP isomers by approximately 40% for all metals, excluding the group IB metals. For the IB metals, the isomer stability

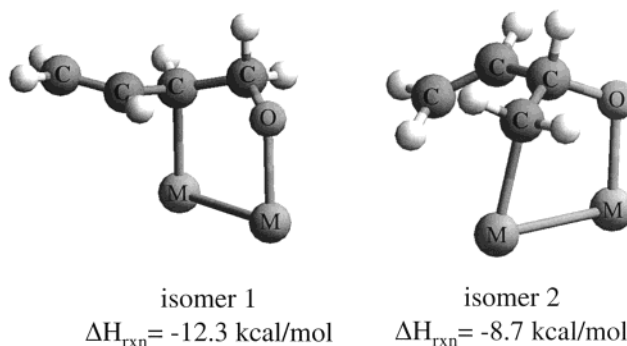


Figure 6. Optimized structures of epoxybutene (EpB) oxametallacycle isomers.

difference for OMMPs has been calculated to be approximately 35% greater than that for OMMIs.

We propose that the reason for the enhanced stability of isomer 2 is related to the degree of methyl substitution at the oxametallacycle carbon atom adjacent to oxygen. This idea can be understood in terms of an analogy to basic organic chemistry. For example, one potential reaction product of OMMI isomer 2 oxametallacycles is acetone; the analogous product for OMMP isomer 1 oxametallacycles is propionaldehyde.^{9,15,28} Acetone, which has a higher degree of substitution at the carbonyl group, is more stable than propionaldehyde by 7 kcal/mol. This enhanced stability is due to the stabilizing influence of alkyl substituents upon the C–O dipole. By analogy with their carbonyl-containing reaction products, OMMI isomer 2 would be expected to be more stable than OMMP isomer 1 because of the higher degree of methyl substitution at the α carbon. For the same reason, OMMI isomer 2 is more stable than OMMI isomer 1. In this case, the substitution of two methyl groups at the alpha position would be expected to further enhance the stability of isomer 2 with respect to isomer 1. This is consistent with the observation that the stability gap between OMMI isomers is in general 40% greater than that for OMMP isomers. The consistency of relative oxametallacycle stabilities (independent of the metal) with stabilities of carbonyl products is not surprising, since the difference between isomer 1 and isomer 2 is in the structure of the organic ligand, not the metal.

To test whether the enhanced stability of α -substituted structures can be generalized to other hydrocarbon substituent groups, we have calculated the stability of different oxametallacycle isomers expected to be formed during synthesis or reaction of 3,4-epoxy-1-butene (EpB) on Ag dimers. This molecule is of particular interest because of the recent commercialization of a silver-catalyzed butadiene epoxidation process by Eastman Chemical.²⁹ The two optimized oxametallacycle structures, along with their calculated stability values, are shown as Figure 6. For EpB-derived oxametallacycle isomers 2 and 1, a vinyl group has been substituted at the α and β positions, respectively. In sharp contrast to our results for methyl substituted oxametallacycles, isomer 1 EpB-derived oxametallacycles are more stable than their isomer 2 counterparts by 3.6 kcal/mol. One possible reason for the stabilization of isomer 1 is that this structure allows for a better partial conjugation of the C–C double bond with the carbon atoms of the oxametallacycle. This increased conjugation would be expected to provide more uniform C–C bond lengths for the three C–C bonds of the oxametallacycle. This was indeed the result of the calculations; the standard deviation of these calculated bond distances is 0.08 Å for isomer 1 compared to 0.10 Å for isomer 2. Furthermore, Mulliken population analysis of the electronic charge for each atom reveals a more uniform charge distribution

for isomer **1** EpB-derived oxametallacycle structures. The gross charge difference between the two backbone carbon atoms of the oxametallacycle was calculated to be 0.34 for isomer **1**, compared to 0.61 for isomer **2**. This result is again consistent with isomer **1** providing a more conjugated (and thus more stable) structure. The enhanced stability for isomer **1** EpB-derived oxametallacycles on Ag indicates that these isomers may be preferentially formed during ring-opening reactions of EpB.

Although our calculations clearly indicate that isomer **2** is the more stable structure for OMMPs and OMMIs, the stability difference between the two isomers is small. On the basis of thermodynamic considerations alone, one might expect products corresponding to isomer **2** oxametallacycles to be preferentially formed during reaction. However, the stabilities of the oxametallacycle isomers are close enough that one must consider other factors that could affect reaction selectivity. For example, modifications of the catalyst surface could influence selectivity by preferentially stabilizing a particular oxametallacycle isomer or associated transition state. Furthermore, if the kinetic barriers to conversion of oxametallacycle intermediates vary significantly, the most abundant intermediate may not give rise to the most abundant product.³⁰ Given their very similar stabilities, it also seems likely that both oxametallacycle isomers could function as intermediates in epoxide ring opening and olefin oxidation reactions, leading to the formation of several isomers as reaction products. Comparisons with the limited database of experimental results for these reactions confirms this conjecture.

Comparisons with Experiment

In studies of supported metal catalysts, oxametallacycles have been proposed as intermediates in the hydrogenolysis of propylene oxide and butylene oxide.^{15,27} On reduced Pd, Pt, Cu, and Ni catalysts, ketones and secondary alcohols are the major products with only small amounts of aldehydes and primary alcohols detected.^{16,17} This product spectrum indicates a preference for formation of isomer **2** during reaction. This result is consistent with oxametallacycle stability being the dominant influence on regioselectivity. However, the primary products of propylene oxide hydrogenolysis reactions over oxidized Ni and Cu catalysts are aldehydes and primary alcohols, indicating that formation of isomer **1** type oxametallacycles is preferred under these conditions. In this case, the presence of oxygen on the catalyst surface has a dramatic effect, reversing the regioselectivity to favor the product associated with the less stable oxametallacycle isomer. It is possible that adsorbed oxygen withdraws electron density from the metal surface, resulting in a more electrophilic catalyst. On electrophilic catalysts, cleavage of the C–O bond at the more substituted end of the epoxide ring is favored.³¹ This is probably due to the stabilization of the transition state via inductive donation from the methyl group attached to the epoxide ring. This concept of transition-state stabilization is consistent with the selectivity pattern observed in the Pd-catalyzed propylene oxide hydrogenolysis over metals on acidic supports; again, isomer **1** type products are formed in much greater abundance.^{32,33} Thus, on the reduced metal, the regioselectivity of propylene oxide hydrogenolysis tracks oxametallacycle stability; however, modification of the surface by increasing the Lewis acidity reverses the observed regioselectivity pattern presumably by lowering the energy of the associated transition state.

Curiously, surface science studies on Rh(111) single crystals show the opposite regioselectivity trend for reactions proposed to involve oxametallacycles. As noted above, Xu and Friend have proposed that oxametallacycles containing methyl groups

bound to the bridging carbon are formed during the oxidation of propylene and isobutylene on Rh(111)-p(2 × 1)-O.^{9,10} In both cases, surface oxygen is proposed to attach to the methyl substituted end of the double bond, resulting in the formation of oxametallacycles analogous to the isomer **2** structure of OMMPs and OMMIs. The formation of isomer **2** rather than isomer **1** oxametallacycles is indicated by the observation that propylene is selectively oxidized to form only acetone and that isobutylene is selectively oxidized to form only tertiary butanol; neither propionaldehyde nor isobutanol was produced. In contrast, Brown and Barteau⁵ proposed the formation of an oxametallacycle containing methyl groups attached to the surface-bound carbon during the decomposition of propylene oxide on the Rh(111) surface. This oxametallacycle corresponds to the OMMP isomer **1** structure, which was predicted to be the less stable isomer in our DFT calculations. Since the routes to oxametallacycles in these two experiments differ (olefin oxidation vs epoxide ring opening), it is not unreasonable that the apparent selectivity of the two reactions might differ. In particular, the preference for ring opening of propylene oxide via the less stable isomer on Rh(111) suggests that the regioselectivity of this reaction is controlled by the kinetics rather than the thermodynamics of oxametallacycle formation. The relatively small differences in isomer stabilities calculated in the present study may be taken as an indication that additional examples of kinetic control of epoxide ring-opening regioselectivity are to be expected on other transition metal surfaces.

The most germane examples connecting oxametallacycles to epoxidation catalysis come from studies carried out on the Ag-(110) surface. Brainard and Madix⁸ have proposed that *tert*-butoxide groups react at 510 K on Ag(110) via a transient oxametallacycle intermediate to form isobutylene oxide and isobutylene. The proposed oxametallacycle has a structure analogous to an OMMI isomer **2** oxametallacycle. This work provides a potentially important link between oxametallacycles and epoxides on Ag surfaces. Unfortunately, under the conditions of the experiment the proposed OMMI oxametallacycle is not a stable intermediate and could not be spectroscopically identified. Brainard and Madix propose that the oxametallacycle is not stable at the elevated temperature (510 K) at which it is formed. We have calculated that the OMMI species is stable with respect to its epoxide by a modest 11 kcal/mol on a 12-atom Ag(110) cluster, supporting the assertion that OMMIs are insufficiently stable to be isolated at 510 K.

The first spectroscopic identification of a stable oxametallacycle on a metal surface was recently reported¹² on Ag(110). Oxametallacycles corresponding to OMME structures decompose at 340 K to form the major products γ -butyrolactone (GBL) and acetaldehyde. DFT-based frequency calculations, used in identifying this intermediate as an oxametallacycle, have predicted a vibrational mode at 717 cm⁻¹ that appears to be a possible reaction coordinate for ring closure to form ethylene oxide. However, ethylene oxide was not observed as a reaction product. Instead, it is proposed that α C–H bonds on the bridging carbon of the OMME are broken in the rate-determining step to form GBL and the other products. As noted above, these α C–H bonds are especially reactive because of their proximity to oxygen. By this reasoning, isobutylene oxide would be the preferred product of the reaction of the OMMI isomer **2** structure because there are no α -hydrogens to eliminate; they have been replaced by methyl groups. Elimination of methyl groups is much less facile on silver catalysts, allowing the OMMI to react to form the epoxide. We have performed DFT-based frequency calculations on the OMMI isomer proposed

to be intermediate in the formation of isobutylene oxide. These calculations have revealed a vibrational mode at 739 cm^{-1} that corresponds to a possible reaction coordinate for ring closure to form the epoxide. Because the absence of α -hydrogens precludes the formation of a cyclic ester like GBL, this DFT-predicted vibrational mode may represent the reaction coordinate for oxametallacycle conversion to isobutylene oxide.

Conclusions

We have used DFT-based methods to evaluate the stability of OMMP and OMMI oxametallacycles for a range of late-transition metals. The relative stability of different isomers of these oxametallacycles has potential implications for the regioselectivity of reactions that proceed via oxametallacycle intermediates. As expected, these results indicate that stability trends across the periodic table remain practically unaffected by the attachment of methyl groups to the oxametallacycle backbone. Relative thermodynamic stabilities of oxametallacycles generally increase as one proceeds leftward and upward in the periodic table. Our results also demonstrate that oxametallacycles containing methyl groups bound to the bridging carbon are slightly stabilized with respect to their isomers, oxametallacycles that incorporate methyl groups bound to the surface-bound carbon. However, because the thermodynamic preference for the former type of oxametallacycle is small, relatively small changes in reaction conditions (such as surface modification with oxygen) may have a greater impact than oxametallacycle thermodynamics on regioselectivity. While one can find a number of examples in which the regioselectivity of surface reactions is consistent with the formation of the more thermodynamically favorable oxametallacycle intermediate, it is clear that a comprehensive description of this chemistry, either from theory or from experiment, is not yet at hand.

Acknowledgment. We gratefully acknowledge the support of the Division of Chemical Sciences, Office of Science, U.S. Department of Energy (Grant FG02-84ER13290). We also thank Professor W. N. Delgass for helpful discussions of our results

and of olefin epoxidation catalysis. J.W.M. acknowledges support from a National Science Foundation Graduate Fellowship.

References and Notes

- (1) Serafin, J. G.; Liu, A. C.; Seyedmonir, S. R. *J. Mol. Catal.* **1998**, *131*, 157.
- (2) van Santen, R. A.; Kuipers, H. P. C. *Adv. Catal.* **1987**, *35*, 265.
- (3) Houtman, C. J.; Barteau, M. A. *J. Catal.* **1991**, *130*, 528.
- (4) Brown, N. F.; Barteau, M. A. *Langmuir* **1992**, *8*, 862.
- (5) Brown, N. F.; Barteau, M. A. *Surf. Sci.* **1993**, *298*, 6.
- (6) Brown, N. F.; Barteau, M. A. *J. Phys. Chem.* **1994**, *98*, 12737.
- (7) Brown, N. F.; Barteau, M. A. *J. Phys. Chem.* **1996**, *100*, 2269.
- (8) Brainard, R. L.; Madix, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 3826.
- (9) Xu, X.; Friend, C. M. *J. Am. Chem. Soc.* **1991**, *113*, 6779.
- (10) Xu, X.; Friend, C. M. *J. Phys. Chem.* **1991**, *95*, 10753.
- (11) Xu, X.; Friend, C. M. *Langmuir* **1992**, *8*, 1103.
- (12) Jones, G. S.; Mavrikakis, M.; Barteau, M. A.; Vohs, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 3196.
- (13) Mavrikakis, M.; Doren, D. J.; Barteau, M. A. *J. Phys. Chem. B* **1998**, *102*, 394.
- (14) Barteau, M. A.; Madix, R. J. *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*; King, D. A., Woodruff, D. P., Eds.; Elsevier: Amsterdam, 1982.
- (15) Bartok, M. *Stereochemistry of heterogeneous metal catalysis*; Wiley: New York, 1985.
- (16) Notheisz, F.; Molnar, A.; Zsigmond, A. G.; Bartok, M. *J. Catal.* **1986**, *98*, 131.
- (17) Notheisz, F.; Bartok, M.; Zsigmond, A. G. *React. Kinet. Catal. Lett.* **1986**, *29*, 339.
- (18) Baerends, E. J.; Elis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.
- (19) Boerrigter, P. M.; te Velde, G.; Baerends, E. J. *Int. J. Quantum Chem.* **1988**, *33*, 87.
- (20) Baerends, E. J.; Ros, P. *Quantum Chem. Symp.* **1978**, *12*, 169.
- (21) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
- (22) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (23) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
- (24) Chase, M. W. *J. Phys. Chem. Ref. Data, Monogr.* **1998**, *9*, 1.
- (25) Heinemann, C.; Hertwig, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 495.
- (26) Brainard, R. L.; Madix, R. J. *Surf. Sci.* **1989**, *214*, 396.
- (27) Besenbacher, F.; Norskov, J. K. *Prog. Surf. Sci.* **1993**, *44*, 5.
- (28) Senechal, G.; Cornet, D. *Bull. Soc. Chim. Fr.* **1971**, 773.
- (29) Monnier, J. R. *Stud. Surf. Sci. Catal.* **1997**, *110*, 135.
- (30) Gates, B. C. *Catalytic Chemistry*; Wiley: New York, 1992.
- (31) Bartok, M. *Acta Chim. Acad. Sci. Hung.* **1976**, *88*, 395.
- (32) Bartok, M.; Notheisz, F.; Kiss, J. T. *J. Catal.* **1981**, *68*, 249.
- (33) Davidova, H.; Kraus, M. *J. Catal.* **1979**, *61*, 1.