lated from k^s_1 according to eq 4) in order to find the best agreement of simulated and experimental curves. Another possible procedure, yielding the same results, is to perform the simulation experiments for different values of k_1, to calculate k_{-1} from k_1 in agreement with eqs 4 and 6, i.e.

$$k_{-1} = k_1(k'_A + 1)/(k'_B + 1) = k_1 t_{R_A}/t_{R_B} \tag{i}$$

initially assuming the same rate constants in both phases, i.e., $k^m = {}^1/_2(k^s_1 + k^s_{-1}) = {}^1/_2(k_1 + k_{-1})$, in order to obtain k_1 and k_{-1}, and then to evaluate according to eq 6. $\Delta G^‡$ was calculated from the corresponding rate constant k (mean of forward and backward reaction) according to the Eyring equation

$$k = f\frac{k_B T}{h} e^{-\Delta G^‡/RT} \tag{ii}$$

where the transmission coefficient is $f = 0.5$ for two consecutive inversions[23,26] (cf. remarks in the text). An estimated error is given for the $\Delta G^‡$ values.

Determination of Retention Increases R'. The retention increases R' were determined by using an achiral OV-1701 reference column, using n-octane as a reference standard, as previously described in detail.[7,28,29]

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Metallaoxetanes as Possible Intermediates in Metal-Promoted Deoxygenation of Epoxides and Epoxidation of Olefins

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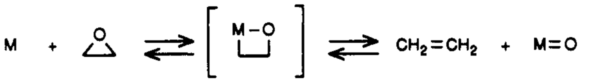
Abstract: Calculations including electron correlation have been performed for the insertion of a number of first and second row transition metal atoms (Cr, Co, Fe, Ni, Cu, Mo, Ag) into the C–O bond of ethene oxide. It is found that for all these metals, except silver, a metallacycle is more stable than the [metal + epoxide]. The energy of [metal + epoxide] is also compared to [metal oxide + ethene] and it is found that only for copper and silver is [metal + epoxide] lower in energy than [metal oxide + ethene]. The difference between the metals in this respect is explained by the difference in binding energy of the diatomic metal oxides. Silver and copper have much weaker M=O bonds than the rest of the metals studied, and this favors an epoxidation reaction.

Metallaoxetanes have been postulated as intermediates in epoxidation reactions with oxotransition metal complexes[2-4] and in metal-promoted deoxygenation of epoxides[2,5] (eq 1). Furthermore, they are likely intermediates in metal-catalyzed insertion of CO_2 into epoxides[6-8] and in the conversion of ketones to alkenes by metal–carbenes.[9-11] Several metallaoxetane complexes have been characterized,[11-13] and recently a ferraoxetane was observed in the matrix reaction between atomic iron and ethene oxide in argon at 12.5–15 K.[13]



(1)

Table I. Calculated Energies in kcal/mol, Relative to the Ground State of the Metal Atom and Free Epoxide

metal atom	ground state	2-metalla-oxetane state	2-metalla-oxetane ΔE	open structure state	open structure ΔE	metal oxide + ethene state	metal oxide + ethene ΔE
Cr	$^7S(d^5s)$	$^5A'$	−32			$^5\Pi$	−14
Fe	$^5D(d^6s^2)$	$^5A'$	−36	$^5A'$	+10	$^5\Sigma^+$	−16
		$^3A'$	−19				
Co	$^4F(d^7s^2)$	$^4A'$	−34	$^4A''$	+7	$^4\Delta$	−15
		$^2A''$	−30				
Ni	$^3D(d^9s)$	$^1A'$	−50	$^3A'$	−3	$^3\Sigma^-$	−18
Cu	$^2S(d^{10}s)$	$^2A'$	−17	$^2A'$	+3	$^2\Pi$	+13
Mo	$^7S(d^5s)$	$^5A'$	−35			$^5\Pi$	−26
Ag	$^2S(d^{10}s)$	$^2A'$	+12	$^2A'$	+17	$^2\Pi$	+35

In this paper we have performed quantum chemical calculations on 2-metallaoxetanes for a number of transition metals (Cr, Mo, Fe, Co, Ni, Cu, Ag) and compared the energy of the metallacycle with the energies of [metal + epoxide] and [metal oxide + ethene]. There are two important questions that we would like to address with these calculations: (i) is the metallaoxetane a likely intermediate in the transformations given in eq 1 and (ii) which is the preferred decomposition pathway for the metallacycle for a certain metal (epoxide or olefin).

The structure of the metallaoxetane used for the calculations is planar, and the geometrical parameters were optimized for the

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Table II. Mulliken Populations for the Different Structures, Charge and Valence d Population on the Metal Atom, Charge on Oxygen

	2-metallaoxetane				open structure				metal oxide + ethene		
metal	state	q_M	d	q_O	state	q_M	d	q_O	state	q_M	d
Cr	$^5A'$	+0.50	4.63	−0.39					$^5\Pi$	+0.21	4.60
Fe	$^5A'$	+0.45	6.32	−0.41	$^5A'$	+0.32	6.24	−0.18	$^5\Sigma^+$	+0.23	6.10
	$^3A'$	+0.30	6.75	−0.30							
Co	$^4A'$	+0.40	7.40	−0.37	$^4A''$	+0.29	7.48	−0.18	$^4\Delta$	+0.17	7.37
	$^2A''$	+0.23	7.90	−0.28							
Ni	$^1A'$	+0.16	8.94	−0.25	$^3A'$	+0.26	8.56	−0.18	$^3\Sigma^-$	+0.12	8.59
Cu	$^2A'$	+0.29	9.61	−0.33	$^2A'$	+0.29	9.76	−0.18	$^2\Pi$	+0.37	9.68
Mo	$^5A'$	+0.52	4.70	−0.45					$^5\Pi$	+0.35	4.54
Ag	$^2A'$	+0.45	9.89	−0.36	$^2A'$	+0.39	9.93	−0.19	$^2\Pi$	+0.41	9.98

nickelaoxetane. For the other first row metals the nickel structure was used and for the second row metals, which are expected to have longer metal–ligand distances than the first row metals, the metal–carbon and metal–oxygen distances were reoptimized. For some of the metals an open structure with only one carbon bound to the metal was also investigated. For most metallacycles and for most metal oxides at least two different spin states were considered. The main comparisons in this paper will be made using the ground state of each structure. The calculations performed include the effects of dynamic correlation of all valence electrons, and the basis sets used are of standard quality including diffuse d functions on the metals. Further details concerning the calculations are given in the Appendix.

Results

The calculated energies are summarized in Table I and Figure 1, and the Mulliken populations are given in Table II.

The calculations indicate that formation of metallaoxetane from epoxide and a metal atom is exothermic for all of the metals studied except silver (Table I and Figure 1). Nickel has the strongest bound metallacycle, 50 kcal/mol more stable than [epoxide + metal]. For chromium, cobalt, iron, and molybdenum the energy gain from the insertion of the metal atom into the epoxide is 30–40 kcal/mol and for copper 17 kcal/mol.

In all cases the metallaoxetane is more stable than the [metal oxide + ethene]. This is particularly pronounced for silver, copper, and nickel, for which the energy difference between [metal oxide + ethene] and metallaoxetane is 23–32 kcal/mol. For these metals it seems likely that the metal oxide would react with ethene and give a metallacycle even if one considers that the [metal oxide + ethene] is stabilized by the formation of a π-olefin complex prior to the formal [2 + 2] addition. For the rest of the metals the calculated energy difference between the metallacycle and metal oxide plus ethene is smaller.

The calculated energies for the two systems [metal + epoxide] and [metal oxide + ethene] suggest that for chromium, cobalt, iron, nickel, and molybdenum the equilibrium shown in eq 1 would lie to the right. For copper and silver the thermodynamics would favor the left side, so that the metal oxide would epoxidize the olefin. It should be noted that the difference between the metals regarding the thermodynamics of reaction 1 is determined by the difference in binding energy for the diatomic metal oxides, so that for the metals with stronger M=O bonds the deoxygenation reaction should be exothermic. In this respect our results are in good agreement with the experimentally known binding energies for the metal oxides.[14] Molybdenum, which has a large binding energy for the oxide, 5.8 eV, has the most exothermic reaction with a ΔE of −26 kcal/mol. For chromium, cobalt, iron, and nickel, which all have the oxides bound by 3.9–4.4 eV, the exothermicity of reaction 1 lies in the range 15–18 kcal/mol. Copper and silver have weaker bound metal oxides, 2.8 and 2.3 eV, respectively, and for these metals reaction 1 is calculated to be endothermic.

Below we will discuss the electronic structure for the different molecular structures, together with the energetics in some more detail.

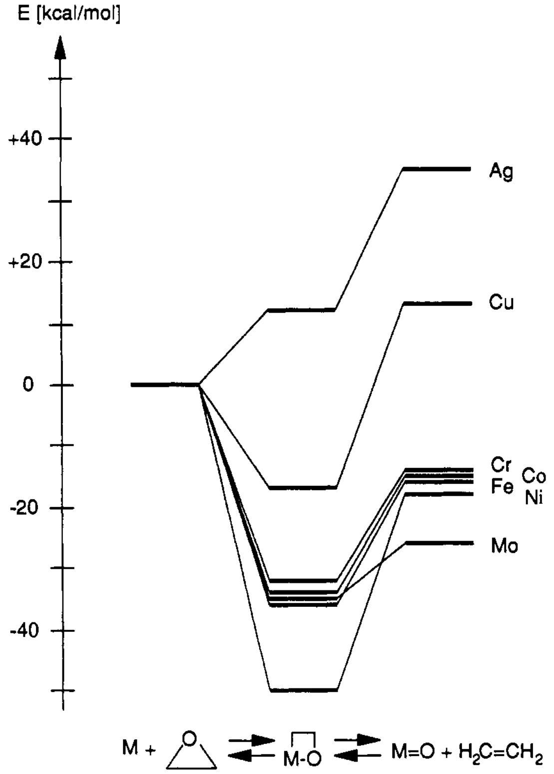

Figure 1. Calculated energies in kcal/mol, relative to the ground state of the metal atom and free epoxide.

a. Metallaoxetanes. The optimal bonding situation in the metallacycles is obtained if two covalent bonds can be formed by the metal, one to the oxygen and one to the carbon. The bonding electron configuration on the metal therefore has to have two open shells. Further, because of the ring structure, the two bonds have to form an angle of about 90°; and the best bonding atomic configuration on the metal therefore has the valence occupation $d^{n+1}s^1$, i.e., the two covalent bonds are formed by one s and one d electron from the metal. The corresponding state on the atom with the lowest energy will have a high-spin coupling of these two electrons, while the metallacycle will have a spin state two steps lower than that of the atomic metal. For the nickel atom the ^3D ground state has the d^9s^1 occupation, which leads to a strongly bound $^1A'$ state of the metallacycle, 50 kcal/mol relative to the metal atom plus epoxide. The Mulliken populations, given in Table II, show that the d^9s^1 configuration is the dominating bonding configuration, the nickel 3d population in the metallacycle being 8.94 electrons. For chromium and molybdenum the atomic ground states (^7S) also have the $d^{n+1}s^1$ occupation (d^5s^1), and the populations in Table II show that for these metals the $d^{n+1}s^1$ state dominates in the metallacycle, the metal d populations being about 4.7 electrons. For chromium and molybdenum, however, the binding energy relative to the metal atom plus epoxide is smaller than for nickel about 35 kcal/mol compared to 50 kcal/mol, which is an effect of a larger loss of exchange energy upon bond formation for the metals with many open shells.[15] Further, it is likely

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that the binding energy of molybdenum is underestimated by a few kcal/mol, since the structure of the metallacycle for molybdenum is less optimal than for the first row atoms.

Silver and copper also have $d^{n+1}s^1$ occupations of the atomic ground states, $^2S(d^{10}s^1)$, but the filled valence d shell implies that no d bond can be formed for these metals. This is the reason why these metals have the least stable metallacycle, the $^2A'$ state of the copper metallacycle being bound by only 17 kcal/mol relative to the metal atom plus epoxide and the $^2A'$ state of the silver metallacycle being unbound by 12 kcal/mol. These metals form one covalent bond using the s electron on the metal, and for silver this is the only bonding interaction, with the unpaired electron in the silver metallacycle delocalized over the carbon and oxygen atoms coordinating to the metal. The single covalent bond in the silver metallacycle is not enough to compensate for the broken C–O epoxide bond, making the silver metallacycle unbound. For copper there is actually a second bonding interaction involving one of the copper d orbitals, but since three electrons (two from copper and one from the epoxide) have to reside in the bonding and antibonding orbitals, the net bonding effect is rather small. The unpaired electron in the copper metallacycle is thus antibonding between copper and the epoxide. For copper there is also a contribution from the excited d^9s^2 configuration, as can be seen from the d population of 9.6 electrons, and this configuration can form two covalent bonds via an sp hybridization. For silver the excitation energy to the d^9s^2 state is much larger than for copper, 4.0 eV compared to 1.5 eV,[16] and therefore this configuration cannot contribute to the bonding, leading to a much less stable metallacycle for silver than for copper. The energy difference of 30 kcal/mol between copper and silver for formation of metallaoxetane from metal and epoxide is in accord with the energy difference of 23 kcal/mol between the bent $^2B_2$ states of $Cu(CH_3)_2$ and $Ag(CH_3)_2$ found in ref 17, in particular if one considers that the silver metallacycle probably has a less optimal structure than the copper metallacycle in our calculations.

For cobalt and iron the excited states of the metallacycle, $^2A''$ and $^3A'$, respectively, correspond to the ground $^1A'$ state of the nickel metallacycle, and the dominant bonding configuration is the $d^{n+1}s^1$ state, which for these metal atoms is an excited state, by 0.42 eV for cobalt (^4F, d^8 s^1) and 0.87 eV for iron (^5F, d^7 s^1).[16] Relative to these excited states of the metal atoms the excited states of the metallacycles are bound by 40 kcal/mol, which is rather similar to the nickel case with 50 kcal/mol, while relative to the ground states of the atoms the binding energy is only 20–30 kcal/mol. However, the very low energy of the ground d^ns^2 states of these metals, $^4F(d^7s^2)$ for cobalt and $^5D(d^6s^2)$ for iron, give rise to high-spin coupled ground states of the metallacycles, $^4A'$ for cobalt and $^5A'$ for iron. The d^ns^2 state forms two covalent bonds through an sp hybridization and this gives rise to a linear structure at the metal atom, which is why this type of bonding is not optimal for the metallacycle. The binding energy of the ground-state metallaoxetane for cobalt and iron, about 35 kcal/mol, is therefore somewhat smaller than the binding energy of the nickel metallacycle (50 kcal/mol). It should be noted that cobalt and iron together with copper are the only metals studied here that form stable metallacycles with the same spin as the atomic ground state, which is why these are the only ones that are likely to be observed in atomic beam experiments. This should be the case for iron and cobalt in particular, since they form the most stable metallacycles. As will be discussed later, the ferraoxetane has already been observed in matrix-isolation studies.[13]

In this context it should be noted that the presently calculated binding energy of the $^5A'$ ground state of the iron metallacycle, 36 kcal/mol, is considerably smaller than the value of 150 kcal/mol recently calculated by Swanstrøm and Jørgensen.[18] Swanstrøm and Jørgensen used Møller–Plesset perturbation theory (MP2), and this method is known to be quite unreliable for transition-metal systems. The binding energy of $Ni(CO)_4$, for example, is calculated,[19] using the MP2 method, to be 33% larger than the experimental value and more than 50% larger than more accurate calculated values.[20] The MP2 method also fails completely to describe the electronic spectrum of the nickel atom. Further, if the C–O bond to be broken in the epoxide to form the metallacycle is estimated to be worth about 80 kcal/mol, the binding energy of 150 kcal/mol calculated by Swanstrøm and Jørgensen leads to a value of 230 kcal/mol for the sum of the Fe–C and the Fe–O single bonds in the metallacycle, which is impossible considering the fact that the FeO double bond in the diatomic metal oxide is worth about 100 kcal/mol[14] and the first and second Fe–C bonds in $Fe(CH_3)_2$ are worth 32 and 61 kcal/mol, respectively.[17] Our calculated value of 36 kcal/mol for the binding energy of the metallacycle is much more reasonable, since it leads to an estimated sum of the Fe–C and the Fe–O single bonds in the metallacycle of 116 kcal/mol, to be compared to the sum to the two Fe–C bonds in $Fe(CH_3)_2$ of 93 kcal/mol.[17]

b. Metal Oxides. The $^2\Pi$ states of the copper and silver oxides are the simplest metal oxides to describe. Starting from the neutral atoms the $d^{10}s^1$ state of the metal forms one σ bonding orbital using the metal s electron and one oxygen p electron, and there is one hole in the 4π orbital, which contains the three oxygen p_π electrons. The σ bond has considerable ionic character as can be seen from the Mulliken populations in Table II, the metal having a positive charge of about 0.4 electrons in the copper and silver oxides. For the rest of the metals studied here the holes in the d orbital make varying degrees of π bonding to oxygen possible, besides the σ bonding which is present for all metals. The absence of π bonding in the silver and copper oxides results in a weak M=O bond,[14] only 2.3–2.8 eV compared to >3.9 eV for the rest of the metals (vide supra).

The electronic structure of the metal oxides will not be further discussed here, since it is outside the scope of the present study to perform an accurate study on these diatomic molecules. It is well-known that even much more sophisticated calculations on diatomic transition metal oxides than those performed here, including larger basis sets and multireference correlation methods, give binding energies which are too low by as much as 1–1.5 eV compared to the experimental values.[21] Our main goal is to compare the different metals, and it is expected that the *relative* binding energies of the metal oxides in the present calculations are much more accurate than the *absolute* binding energies, which is corroborated by the fact that the relative positions of the metal oxide plus ethene systems correspond very well to the experimental metal oxide binding energies as discussed above.

c. Open Structures. For iron, cobalt, nickel, and copper an open structure corresponding to nucleophilic attack by the metal atom on the epoxide ring was also investigated. In this structure one covalent bond is formed between the metal and one of the carbons, and the optimal electronic configuration on the metal is, as for the metallacycles, $d^{n+1}s^1$. The σ bond is formed mainly by the s electron on the metal and one p electron on carbon. Both nickel and copper have the same $d^{n+1}s^1$ configuration as the atomic ground state, and the binding energy of the open structure is about the same for these two metals, bound by 3 kcal/mol for nickel and unbound by 3 kcal/mol for copper. Since these values are close to zero, the metal–carbon bond in this structure is apparently of about the same strength as the C–O bond which was broken in the epoxide. Iron and cobalt have d^ns^2 ground states, and since the s electrons are outside the d electrons this state cannot efficiently form a covalent bond to carbon. Therefore, these metals have to involve one or both of the excited states $d^ns^1p^1$ and $d^{n+1}s^1$, which makes the open structure less stable for iron and cobalt than for nickel and copper. For all the metals the open structure has one unpaired electron localized on oxygen, in a p orbital lying in

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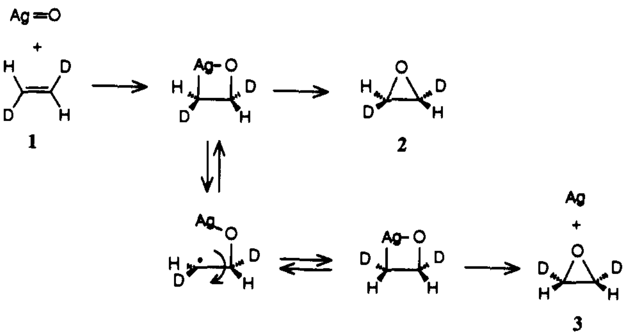
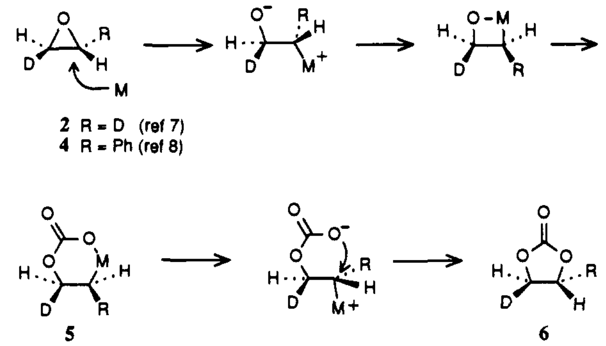
Scheme I



Scheme II



the M–C–C–O plane, and perpendicular to the C–O bond. For copper, with ten d electrons, this is the only unpaired electron, and for nickel, cobalt, and iron there are additionally one, two, or three unpaired metal d electrons, respectively, on the metal.

Discussion

A number of oxometal complexes are known to epoxidize olefins,[2a,3,4] and metallaoxetanes have been inferred as likely intermediates. In the heterogeneous silver-catalyzed epoxidation of ethene by molecular oxygen[3,22,23] it is generally agreed that an oxosilver surface is responsible for the oxygen transfer to the double bond.[22,24] The calculated energies for the silver metallacycle and [Ag=O + ethene] being 12 and 35 kcal/mol above [Ag + epoxide] are in agreement with these experimental findings. The stereochemistry of the silver-catalyzed epoxidation of (*E*)-1,2-dideuterioethene **1** has been investigated (Scheme I), and it has been observed that the relative yield of retention product **2** varies from 70% to 55%.[23] The considerable stereorandomization observed would at first glance seem to contradict the formation of an intermediate metallacycle. However, the fact that the calculated energy is quite high for the argentaoxetane indicates that it should be labile. An opening of the ring could therefore occur with concomitant rotation of the carbon–carbon bond which would lead to the observed loss of stereospecificity (Scheme I).

The present results for chromium, yielding a lower energy for [chromium oxide + ethene] than for [chromium atom + epoxide], seems to contradict previous experimental and theoretical observations that oxochromium complexes epoxidize olefins.[2] However, the previous results[2] were obtained for high valent dioxochromium complexes, and it has been shown in theoretical investigations[25] that the second oxygen ligand plays an important role for the relative stability of different parts of the potential surface in the epoxidation reaction. The relative positions of the left and right hand sides of eq 1 are determined by the strength of the diatomic metal oxide bond, and the strong Cr=O bond (4.4 eV[14]) forces the reaction 1 to the right hand side in the chromium case. However, the second oxygen in dioxochromium complexes is expected to be less strongly bound than the first one, and therefore the transfer of an oxygen ligand from such complexes to ethene is expected to be more favorable than from the monooxide studied in the present paper. The present results are consistent with the fact that lower valent tungsten complexes deoxygenate epoxides to give a monooxometal complex + olefin.[5,26] Interestingly the latter reaction is stereospecific, with (*Z*)-epoxide giving (*Z*)-olefin.

In matrix experiments it has been shown that a beam of iron atoms reacts spontaneously with ethene oxide, and by the use of FTIR spectroscopy the product was determined to be an iron metallacycle, the first unligated metallaoxetane.[13] The present results agree well with these experimental observations, since the $^5A'$ ground state of ferraoxetane is calculated to be 36 kcal/mol more stable than the ^5D ground state of the iron atom and epoxide. The calculations further predict that it should be possible to observe the same type of product also for cobalt atoms, since the $^4A'$ ground state of cobaltoxetane is found to be bound by 34 kcal/mol relative to the ^4F ground state of the cobalt atom. For nickel, chromium, and molybdenum, on the other hand, the ground state of the metallacycle does not correlate with the ground state of the metal atom, since the atom has a higher spin state than the metallacycle. Therefore the insertion of ground-state metal atoms into the C–O bond of epoxides is not expected for these metals, even though the metallacycles are quite stable.

For nickel and copper the rather low energy of the open structure (Table I) indicates that this structure could be an intermediate in the reaction of the metal and epoxide to give a metallaoxetane. An S_N2-type attack by the metal on the carbon followed by rotation around the carbon–carbon double bond and formation of a metal–oxygen bond would give the metallacycle. Stereochemical studies would be necessary to distinguish this S_N2-type oxidative addition from a three-center oxidative addition of the carbon–oxygen bond to the metal. Studies of the reaction of specifically deuterated epoxide (**2** and **4**), CO_2 and copper(I),[7] nickel(0),[7] or platinum(II)[8] complexes have shown that the cleavage of the C–O bond by the metal is stereospecific for copper and platinum but nonstereospecific for nickel. In the copper case formation of a cyclic carbonate **6** from epoxide **2** with retention of the overall stereochemistry can be interpreted as a double inversion involving an S_N2-type oxidative addition (Scheme II).[7] In the platinum case an S_N2-type oxidative addition with inversion at carbon was unambiguously established by the isolation of metallacycle **5**.

Conclusions

The calculations performed here suggest that metallaoxetanes are reasonable intermediates in epoxidation reactions of olefins and in deoxygenation reactions of epoxides. Furthermore, for Cr, Mo, Fe, Co, and Ni the deoxygenation reaction seems to be favored, whereas for Cu and Ag the epoxidation is preferred (cf. eq 1). The calculations also provide an explanation for the varying stability of the different metallaoxetanes.

Appendix: Computational Details

For the first row metals Wachters (14s, 9p, 5d) primitive basis[27] was used, augmented with a diffuse d function and two 4p functions leading to a (14s, 11p, 6d) primitive basis. The general contraction scheme[28] was used, giving minimal basis in the core and double-ζ in the valence shells. The addition of the diffuse d function on the metals leads to triple-ζ description of the d shell. The contracted basis sets are thus [5s, 4p, 3d]. For the second row metals the Huzinga (17s, 11p, 8d) primitive basis[29] was used, augmented with one diffuse d function and two p functions in the

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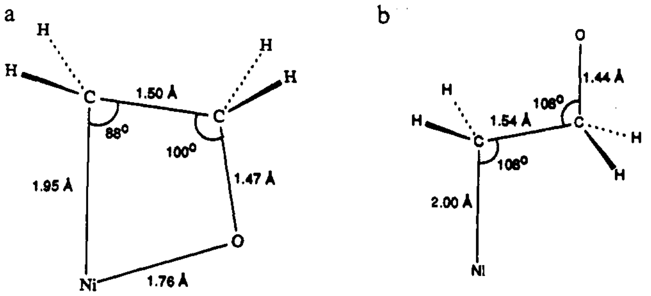

Figure 2. Geometrical parameters optimized for the nickel systems: (a) metallaoxetane and (b) open structure.

5p region, yielding a (17s, 13p, 9d) primitive basis. These basis sets were contracted using the general contraction scheme in a similar way as for the first row metals. For the second row metals, however, the core orbitals 4s and 4p have to be described by a double-ζ basis to reproduce the relativistic effects[30] leading to a [7s, 6p, 4d] contraction. These basis sets give results close to the Hartree–Fock limit, within 0.05 eV, for the splitting between the lowest atomic states. For carbon and oxygen the primitive (9s, 5p) basis by Huzinaga[31] was used, generally contracted to (3s, 2p). One d function with exponent 0.63 for carbon and 1.33 for oxygen was added. The hydrogens were described by the (4s) basis from ref 31 contracted to [2s] and with the exponents scaled by a factor 1.2.

The correlated calculations were performed using the modified coupled pair functional (MCPF) method[32] which is a size-consistent, single reference state method. For the nickel system a large number of comparisons were made with CASSCF (complete active space SCF) and multireference CI (configuration interaction) calculations. It was found that the single reference MCPF method gives results in good agreement with the multireference calculations, and it was therefore concluded that the MCPF method should give a reliable description of the systems studied here. All valence electrons were correlated, i.e., the 3d and 4s electrons on the first row metals and 4d and 5s electrons on the second row metals together with all electrons on the epoxide unit except the 1s electrons on carbon and oxygen. Relativistic effects were accounted for using first order perturbation theory including the mass-velocity and Darwin terms.[33]

To obtain good agreement with experiment for the splittings between the lowest electronic states of the transition metal atoms very large calculations are needed, including high angular momentum basis functions and long CI expansions. The present calculations give deviations from the experimental splittings of up to 0.5 eV, with the higher d occupations obtaining too high relative energy. To mimimize the error in the calculated interaction energies we have used the following procedure. Since the $d^{n+1}s^1$ state on the metal atoms is the dominating bonding state in most cases studied here, this state was used as reference point to calculate the relative energies for all metals. For those metals that do not have the $d^{n+1}s^1$ state as ground state (iron and cobalt) the experimental atomic splittings were used to obtain the ground state as a reference point. This procedure might produce somewhat too large binding energies for some of the iron and cobalt structures, but since normally too small binding energies are obtained in calculations it is not likely that the iron and cobalt binding energies are overestimated by more than a few kcal/mol.

The geometry for the nickelaoxetane was optimized on the CASSCF[34] level, with the two molecular orbitals forming bonds to nickel, their antibonding counterparts, and one doubly occupied nickel 3d orbital in the active space. The ring geometry was optimized, while the hydrogen parameters were taken from ethene oxide. The most important parameters in the resulting structure, which was found to be planar, are shown in Figure 2a. This geometry was used for all first row transition metals, while for the second row metals the bond lengths were increased to 2.11 Å for Mo–C, 1.91 Å for Mo–O, 2.23 Å for Ag–C, and 2.09 Å for Ag–O. These values were obtained through a partial optimization at the MCPF level.

For the open structure, the geometry for the nickel species was also optimized on the CASSCF level. The two molecular orbitals which are bonding and antibonding between nickel and carbon were placed in the active space, together with the open shell oxygen 2p orbital and two open shell nickel 3d orbitals. The bond lengths of the Ni–C–C–O skeleton, which was forced to be planar, were optimized, while the bond angles and the hydrogen positions were taken from ethanol. The geometry thus obtained was used for the first row metals and is shown in Figure 2b. For silver the Ag–C bond length was increased to 2.23 Å.

For the metal oxides the geometries were optimized on the MCPF level, and the bond lengths obtained for the ground states were 1.63, 1.66, 1.64, 1.62, 1.76, 1.76, and 2.06 Å for CrO, FeO, CoO, NiO, CuO, MoO, and AgO, respectively.

For ethene and ethene oxide the experimental geometries were used.

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