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Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida 32611

Molecular Orbital Investigation of the Oxidation of Olefins by *cis*- and *trans*-Ruthenium(VI)–Dioxo Complexes

Thomas R. Cundari and Russell S. Drago*

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The INDO/1 semi-empirical molecular orbital model is employed to analyze the reaction between olefins and *cis*- and *trans*-Ru(VI)–dioxo complexes. Interesting differences in the reactivity of these seemingly similar complexes toward olefins exist. For the *cis*-Ru^{VI}O$_2$ system, products formed from the cleavage of the C=C double bond (i.e. carbonyls) are obtained. The trans isomer is selective for epoxidations. Three distinct pathways for interaction between the *cis*-RuO$_2$ complex and ethylene were considered—[1 + 2], [2 + 2], and [3 + 2] cycloaddition—as were the intermediates derived from these pathways. The dioxometallacycle is formed from the [3 + 2] pathway. INDO/1 calculations show that the dioxometallacycle is the global minimum for the interaction of ethylene and the *cis*-RuO$_2^{2+}$ complex. Conversion of the dioxometallacycle to epoxide products is energetically unfavorable. For the *trans*-Ru^{VI}O$_2$ complex no dioxometallacycle forms and only epoxides (by a nonconcerted [1 + 2] pathway) are formed.

Introduction

Since the discovery that the reaction of an Fe(III)–porphyrin complex with iodosobenzene (C_6H_5–I–O) could mimic the reactivity of the O_2/cytochrome P-450 system,[1,2] there has been an abundance of research on metal–oxo complexes.[3] Theoretical calculations on this and other related metal–oxo complexes have been carried out.[4] Experimentally, a growing amount of work has been focused on metal–dioxo, M(O)$_2$, compounds;[3,5] theoretically, less attention has been paid to the bonding and reactivity of these complexes.[6] Griffith has derived qualitative rules for predicting which geometric isomer is the most stable as a function of d orbital population for polyoxo complexes.[6b] Jørgensen and Hoffmann have studied the interaction of ethylene with OsO$_4$ using the extended Hückel method.[6f] Rappê and Goddard have used generalized valence bond calculations to study the oxidation of ethylene by various d^0 molybdenyl and chromyl compounds.[6g]

Dioxo complexes are of particular interest for various reasons. First, they are plausible intermediates in the activation of O$_2$ by a single metal center[5b,6c] (eq 1). Ru(II) complexes have been

$$L_nM^q + O_2 \rightarrow L_nM^{q+4}(O)_2 \qquad (1)$$

shown[5a,c] to regenerate the active oxidizing species in the presence of O$_2$ without the need for expensive and difficult to handle oxygen atom transfer reagents.[7] Second, there is an interesting difference in the product distributions for the *cis*- and *trans*-Ru^{VI}(O)$_2$ complexes; the cis complexes[5a] lead to predominantly carbonyl products formed by the cleavage of the C=C double bond; the trans complexes[5b–e] yield epoxides as the major product. Third, many interesting pathways may be envisioned for oxidations involving these dioxo systems arising from the similarity of the *cis*-RuO$_2$ moiety with ozone.

It is the aim of the present research to gain a better understanding of the Ru(VI)–dioxo/organic substrate interaction, to explore comparisons between the Ru(VI)–dioxo and Ru(IV)–oxo complexes, and to investigate the causes of the difference in reactivity between the cis and trans isomers.

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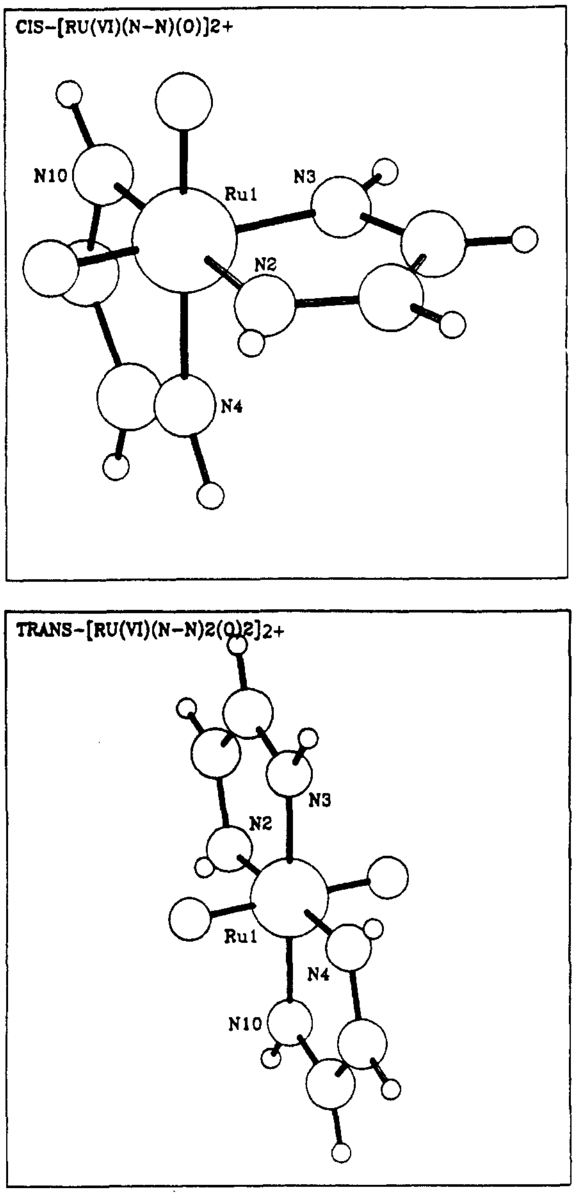

Figure 1. Geometries of the *cis*- and *trans*-$Ru^{VI}(NH{=}CH{-}CH{=}NH)_2(O)_2{}^{2+}$ model complexes used in the present study.

Calculations

The calculations were carried out by using a semi-empirical INDO/1[8] program developed by Professor Michael C. Zerner (Department of Chemistry, University of Florida) and co-workers.[8c,d] The restricted open-shell Hartree–Fock (ROHF) formalism[9] was used for open-shell species. Gradient-driven geometry optimizations[10] were carried out on the various complexes to yield stationary points on the potential energy surface (PES). Convergence to a minimum on the PES was assumed when the gradient was less than 5.0×10^{-3} hartree/bohr. Energies converged well within 0.1 kcal mol^{-1} in all cases. Numerous INDO/1 calculations have been performed for pertinent reference molecules to ascertain the suitability of the INDO/1 model for the description of the bonding in second-row transition-metal compounds.[8d] The results show that the INDO/1 method performs exceptionally well for a variety of calculated properties such as equilibrium geometries, ordering of geometric isomers, atomic charges, orbital energies, etc.[8d] The results for pertinent Ru–oxygen systems have been presented elsewhere.[4b]

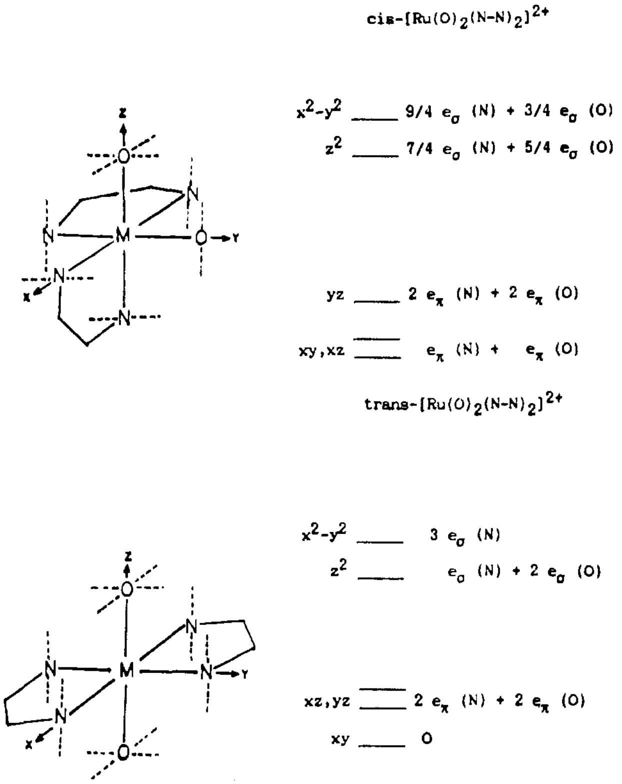

Figure 2. Frontier orbital splitting diagrams derived with the aid of the angular overlap model (AOM) for and *cis*- and *trans*-ML_4O_2 complexes. The vertical and/or horizontal dashed lines represent the orientation of the π-symmetry orbitals in the ligand of interest.

Results

1. Electronic Structure of *cis*- and *trans*-Ru(VI)–Dioxo Complexes. The model complexes used in this present study are *cis*- and *trans*-$[Ru^{VI}(NH{=}CH{-}CH{=}NH)_2(O)_2]^{2+}$ (hereafter referred to as *cis*- and *trans*-$RuO_2{}^{2+}$, Figure 1). *cis*- and *trans*-$Ru^{VI}O_2$ complexes have been employed by various workers for the oxidation of different organic substrates.[5a–e] Optimization of the Ru–O bond lengths in the cis and trans complexes show the equilibrium value to lie near 1.71 Å, in excellent agreement with the values of 1.718 and 1.705 Å reported by Che[5e] for $Ru^{VI}O_2{}^{2+}$ complexes with nitrogen ligands. Geometric details are given in Appendix A. Analogies have been made between monooxo–Ru(IV) complexes and O_2[4b] (with respect to the covalency of the π system and the presence of low-energy singlet and triplet states[11]). Thus, an analogy may be drawn between the Ru(VI)–dioxo complexes and ozone.

The frontier orbital splitting diagrams for the cis-divacant and square-planar ML_4 complexes are well-known.[12] Interaction of these ML_4 fragments with two oxygen atoms each yields the d orbital splitting diagram in Figure 2. The results were derived with the aid of the angular overlap model[12] (AOM) and as such neglects second-order interactions between metal-based AOs of the same symmetry. With this simple picture, predictions about the bonding in d^2 dioxo complexes can be made. There are, however, serious deficiencies in this simple model such as ignoring the repulsion of the d_{xy} by the σ_{CC} of the glyoxal diimine, ignoring $(n + 1)$s and $(n + 1)$p participation, no accounting for electron-electron repulsions, etc. With Figure 2 as a first approximation, the trans isomer is predicted to be more stable due to the lower energy of the HOMO (d_{xy}).[6b] However, an INDO/1 calculation places the cis isomer lower in energy than the trans by 34 kcal mol^{-1}. The reasons for this discrepancy are unclear although it may be attributed to a deficiency in the model complex, the

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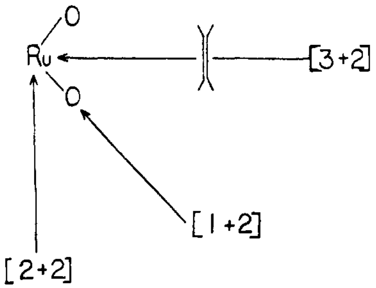

Figure 3. Orientations of ethylene relative to the *cis*-RuO_2 fragment that characterize the [1 + 2], [2 + 2], and [3 + 2] pathways.

INDO/1 method, or a single determinant representation for the ground state of the dioxo complexes. Our extensive work with INDO/1 and Ru–oxo-catalyzed oxidations leads us to believe that the latter problem is the dominant factor. It is interesting to note that including electron correlation crudely (i.e. correlating the four highest occupied and the four lowest unoccupied MOs by using configuration interaction—double excitations) reverses the energy ordering—the trans isomer is now lower by 35 kcal mol^{-1}. The greater correlation contribution for the trans isomer is a result of its frontier orbitals (the highest occupied and lowest unoccupied MOs have significant Ru $d\pi$–O $p\pi$ character) being closer in energy. This leads to lower energy excited configurations and more extensive mixing. One must be careful in applying CI to semiempirical methods such as INDO/1 since the parameters are obtained from experiment (which includes electron correlation). An overcorrection for electron correlation may result. The fact that both *cis*- and *trans*-$Ru^{VI}O_2$ and $Os^{VI}O_2$ complexes have been experimentally determined[3] implies that the d^2, dioxo geometries are close in energy and that factors such as steric repulsions may play an important role in determining the ground-state geometry.

2. *cis*-RuO_2^{2+}/Ethylene Reaction Pathways. The delocalized nature of the π bonding in the RuO_2 moiety, and the analogy with ozone, readily suggests a variety of pathways and intermediates. In this paper the terms *intermediate* and *structure* are used to refer to geometries that do and do not, respectively, represent minima on the PES. Three concerted pathways (and their nonconcerted variants)—[1 + 2], [2 + 2], and [3 + 2]— were considered; they led to the oxo/epoxide (OE), oxo/metallaoxetane (OM) and dioxometallacycle (DM) intermediates, respectively (Figure 3). The [1 + 2] pathway is characterized by the formation of two C–O bonds between the two C atoms of ethylene and one O atom of the dioxo complex. In the [2 + 2] pathway Ru–C and C–O bonds are formed. In the [3 + 2] pathway two C–O bonds are formed between the two C atoms of ethylene and the two O atoms of the dioxo complex. In a concerted pathway, both bonds are formed at the same time; in a nonconcerted pathway, one bond is formed first and then the second is formed.

Initial geometry optimization yielded weakly bound minima on the potential energy surface (PES) similar to those obtained for the Ru(IV)–oxo complexes.[4b] The average distance from the center of the C–C bond of ethylene to the center of the line that connects the two oxos is ≈2.5 Å. The orientation of the ethylene relative to the metal complex does not affect the strength of the binding (≈10 kcal mol^{-1}) as would be expected from a nondirectional electrostatic interaction. The amount of electron density transferred (<0.1 electron) is small, coming chiefly from the olefin π MO. Perturbation of either reactant from their isolated optimized geometries is insignificant. These complexes have recently been advanced by Bruice and Ostovic (referred to as charge-transfer complexes) based on an experimental analysis of Fe-(porphyrin)–oxo-mediated epoxidations.[13] These charge-transfer complexes were obtained regardless of the initial orientation of the olefin relative to the complex as long as the initial separation between the reactants is greater than approximately 2.7 Å.[4b]

A. [1 + 2] Pathway. In the concerted [1 + 2] pathway the olefin is perpendicular to the vector which describes the Ru–O bond. Furthermore, the Ru–O bond vector bisects the center of the C–C bond of the ethylene. Bringing the ethylene along the concerted [1 + 2] pathway, Figure 3, eventually leads to a large repulsion between the ethylene π MO and the oxo lone pair. Single-point INDO/1 calculations (dioxo and ethylene geometries were kept fixed) show that even as far out as $r_{CO} \approx 2.0$–2.5 Å moving the ethylene off the concerted [1 + 2] pathway, i.e., where the Ru–O bond no longer bisects the center of the C–C bond, leads to a lowering of the total energy by decreasing the two-orbital, four-electron repulsion between the oxo lone pair and C_2H_4 π MO. This stabilization gets larger (as a result of greater overlap and hence greater interaction) as r_{CO} approaches covalent values. Deviation of the ethylene from the concerted [1 + 2] pathway causes it to approach the [2 + 2] and [3 + 2] pathways (Figure 3). At large separations, there is no preference for either trajectory. Once this perturbation from the concerted [1 + 2] pathway is induced, formation of the oxo/epoxide can occur in a nonconcerted manner, i.e. one C–O bond forms and then the second as revealed by INDO/1 geometry optimization. An oxo/epoxide intermediate (singlet spin state) was found, by geometry optimization, on the PES with Ru–O bond lengths of 1.84 Å (oxo) and 2.18 Å (epoxide). These results are consistent with experimental values of 1.77–1.86 Å for Ru(IV)–O complexes[5c] and 2.03 and 2.07 Å for *trans*-$[RuCl_4(NO)(OH)]^{2-}$ and *trans*-$[Ru(NH_3)_4(NO)(OH)]^{2+}$, respectively.[14]

B. [2 + 2] Pathway. In the concerted [2 + 2] pathway the olefin C–C and complex Ru–O bonds are parallel, the π MOs point directly at each other. As mentioned above, at large separations between the ethylene and *cis*-RuO_2 translation of the ethylene from a [1 + 2] trajectory toward either a [2 + 2] or [3 + 2] pathway is equally favorable (Figure 3). However, single-point calculations (once again the substrate and oxidant geometries were frozen) show that as the C–O bonds approach covalent values, the [2 + 2] pathway becomes increasingly disfavored in relation to the [3 + 2] pathway. Simple Woodward–Hoffmann considerations state that a concerted, planar [2 + 2] cycloaddition is unfavorable for a four electron system. The Ru–O π bond, as noted above, is highly covalent. Thus, a lowering of the activation energy which causes the "forbiddeness" of the [2 + 2] pathway is not expected. A series of geometry optimization along the [2 + 2] pathway were carried out and did not isolate an intermediate (the oxo/metallaoxetane, OM). An artificially constructed OM is not an optimized minimum on the [2 + 2] pathway. Starting with a reasonable geometry for the oxometallocycle[4b] and then submitting this structure to an INDO/1 geometry optimization show that the structure undergoes further geometric relaxation (and energy lowering) to arrive at a dioxometallacycle intermediate (singlet spin state).

C. [3 + 2] Pathway. In the concerted [3 + 2] pathway the *cis*-RuO_2 moiety of the oxidant and the C atoms of the substrate are coplanar. Also, both C–O distances are equal at all points on the concerted [3 + 2] pathway. A concerted [3 + 2] cycloaddition is an allowed reaction for a six-electron system. The correlation diagram is shown in Figure 4. Notice the correlation of the olefin π MO with a π-symmetry MO (denoted schematically by a p orbital but predominantly $4d\pi$ in character) on the Ru. This leads to the formal two-electron reduction of the Ru(VI)–dioxo complex to yield the d^4 $\overline{\text{O–Ru}^{\text{IV}}\text{O–CH}_2\text{CH}_2}$ intermediate; INDO/1 geometry optimization yields the bond lengths Ru–O = 1.94 Å, C–O = 1.41 Å, and C–C = 1.52 Å. These values are in good agreement with the 2.03 and 2.07 Å Ru–O bond lengths quoted above for the two ruthenium-hydroxy complexes[14a] and the C–O and C–C bond lengths in tetrahydrofuran, C–C = 1.54 ± 0.02 Å and C–O = 1.43 ± 0.03 Å.[14a] The O–Ru–O angle is 81°. As the progress of the geometry optimization was followed, it was observed that the addition is concerted; i.e., both C–O bond lengths are always equivalent.

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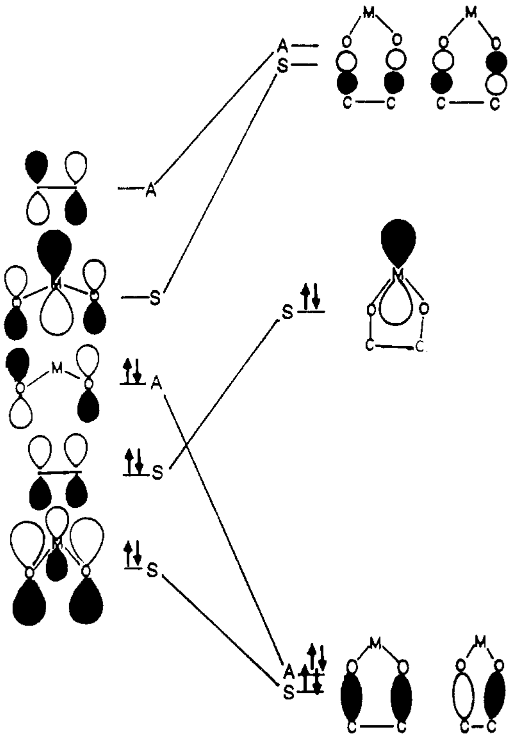

Figure 4. Orbital correlation diagram for the [3 + 2] addition (or 1,3-dipolar addition) of ethylene to a *cis*-RuO_2^{2+} fragment.

The dioxometallacycle is roughly 90 kcal mol^{-1} lower in energy than the oxo/epoxide intermediate. As the OM structure does not represent a stationary point on the potential energy surface, it is not possible to compare the energy of the optimized DM and OE minima with an "artificially" constructed OM.[15] The energies of the two minima, DM and OE, can be rationalized. If the Ru–O bonds are considered to approximately cancel each other out, then the difference in energy between the DM and the OE corresponds to the difference in energy between the C–O bonds formed. In the DM, two unstrained C–O bonds are formed (BE ≈ 85 kcal mol^{-1} [16]); in the OE, two strained, epoxidic C–O bonds are formed (BE ≈ 50 kcal mol^{-1} [17]). Thus, a rough bond energy estimate is 70 kcal mol^{-1}, in qualitative agreement with the INDO/1 result.

3. Interaction of Ethylene with *trans*-$[Ru^{VI}(O)_2(N\text{-}N)_2]^{2+}$. The study of the *trans*-RuO_2^{2+} complex is motivated by the desire to understand the epoxidation system $Ru(TMP)(O)_2$.[5c] As with the monooxo complex, two pathways are envisioned for *trans*-RuO_2^{2+}—a [1 + 2] and a [2 + 2] cycloaddition. It was originally hoped that the effect of the trans ligand on stabilizing the two intermediates—bound epoxide and oxometallocycle—could be studied. However, as with every other Ru–oxo complex we have studied,[4b] a [2 + 2] "intermediate" is not a stable, isolable stationary point on the potential energy surface. Once again, the strength of the Ru–oxo π bond should be regarded as the chief obstacle standing in the way of the [2 + 2] pathway. A bound epoxide intermediate is formed preferentially for the *trans*-$Ru(O)_2$ and *trans*-Ru(O)(THF) complexes. INDO/1 geometry optimization shows that the formation of the bound epoxide is nonconcerted; i.e., one C–O bond is formed first and then the second. The only interesting difference between the two intermediates is the planar (with respect to the Ru–O–C–C atoms) epoxide coordination mode in the former and the nonplanar coordination mode in the latter. Since the d^4 Ru(O)(bound epoxide) complex has a vacant dπ set, the planar coordination mode of the bound epoxide allows for maximum interaction with the epoxide π symmetry nonbonding MO. In the d^6 Ru(THF)(bound epoxide) complex, both dπ orbitals are occupied and the bent coordination mode of the epoxide arises from the desire to keep the repulsive Ru dπ–O pπ interaction at a minimum.

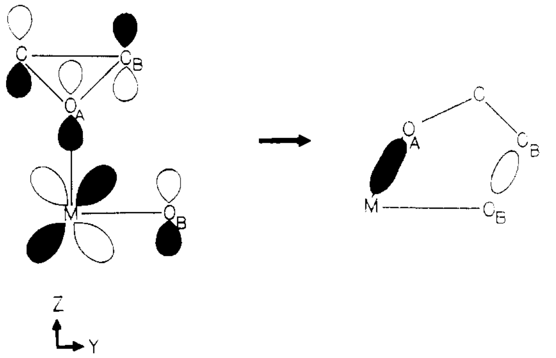

Figure 5. Schematic showing the composition of the HOMO of the *cis*-Ru–oxo/epoxide and the orbital to which it is eventually converted to in the DM. The glyoxal diimine ligands have been removed for clarity, and all atoms shown are coplanar.

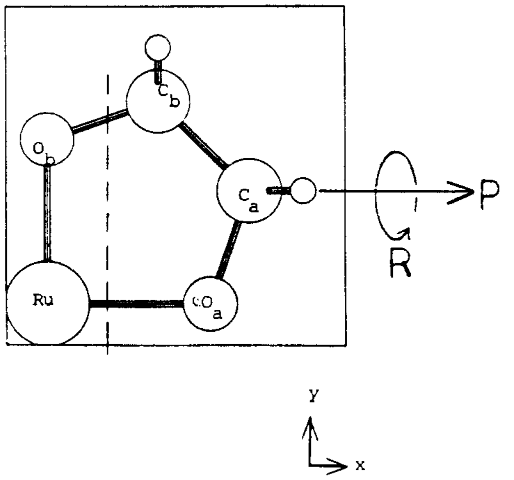

Figure 6. Starting geometry of the dioxometallacycle and the coordinates (*P* and *R*) that were used to construct the PES in Figure 7.

4. Geometric Rearrangement of *cis*-Ru(O)(epoxide) to Ru(dioxometallacycle). The interaction of *cis*-RuO_2 with ethylene yielded two distinct covalently bound minima—the oxo/epoxide (OE) and the dioxometallacycle (DM). The question arises as to whether the formation of the OE is part of competing pathway or a "pit stop" on the way to the more stable dioxometallacycle. A look at the HOMO is informative (Figure 5). This HOMO may be stabilized[18] by increasing the in-phase overlap between the Ru d orbital and the O_a p orbital as well as the in-phase overlap between the C_b p orbital and O_b p orbital. To accomplish this a closing of the O_b–Ru–O_a angle would be the simplest motion. The O_b–Ru–O_a angle was compressed from 90° while other geometric parameters were kept the same. INDO/1 yielded an activation barrier of ≈6 kcal mol^{-1} (O–Ru–O ≈ 64°). An analysis of the wave functions indicates a process involving the concerted breaking of one C–O bond (epoxidic) with the concomitant formation of a stronger C–O bond. Thus, it seems plausible to propose the dioxometallacycle, and the pathway leading to it, as the main route for the oxidation of olefins by a *cis*-$Ru(VI)O_2$ complex. Groves' report[17] of cis/trans epoxide isomerization by a Ru(II)-porphyrin complex is consistent with the notion that the bound epoxide is not "inactive" once it is formed as well as with C–O bond breaking being somewhat facile.

5. Conversion of the Dioxometallacycle to Products. With the dioxometallacycle having been shown to be the most favored intermediate, pathways for its conversion to epoxide products were studied next. For the sake of simplicity, the $\overline{RuOC_2H_4O}$ moiety was made symmetrical (i.e. local C_{2v} symmetry) (Figure 6). A

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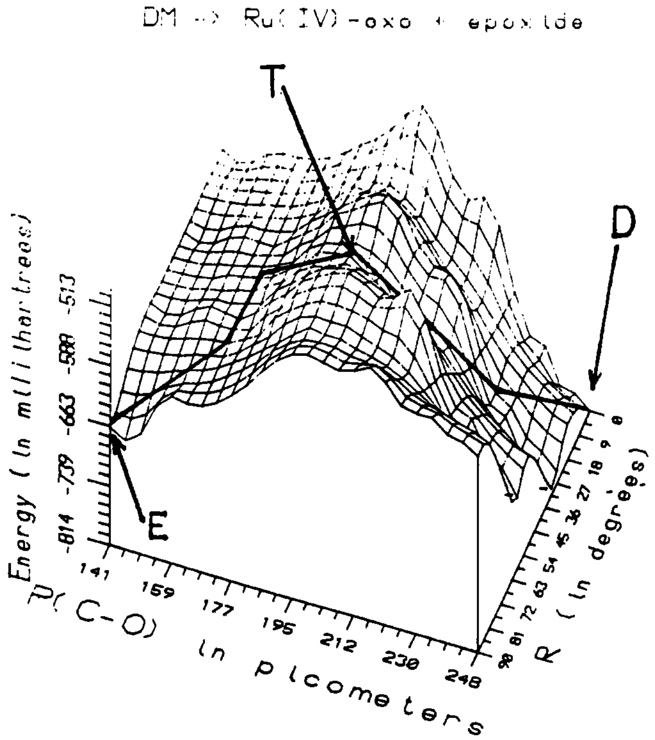

Figure 7. 3D PES constructed for the conversion of the dioxometallacycle intermediate into epoxide products. P (which is measured as the change in the C_b–O_b bond) ranges from 141 to 248 pm, R ranges from 0 to 90°, and E ranges from −138.814 to −138.491 au. E indicates the oxo/epoxide, D is the dioxometallacycle, and T is the transition state that connects them.

potential energy surface, patterned after that used by Purcell in his extended Hückel analysis of peroxometallacycle decomposition ($\overline{\text{M–O–O–C–C}}$, M=Rh(III), Mo(VI)[19]) was constructed. Two independent coordinates characterize this PES: P, a displacement of the $C_2H_4O_a$ fragment parallel to the x axis (Figure 6), and R, counterclockwise rotation of this $C_2H_4O_a$ fragment about an axis passing through C_a and perpendicular to the y axis (Figure 6). There are also two dependent coordinates: a shortening of the Ru–O_b bond (from 1.94 to 1.70 Å) that is necessary when the Ru(IV)–oxo product is formed ($\delta(r(\text{Ru–O}_b)) = -0.02$ Å per 0.1-Å displacement along P) and a closing of the O_a–C_a–C_b angle (from 116° to 57.5°) to form the epoxide ($\delta(\theta(\text{O}_a\text{–C}_a\text{–C}_b)) = -5°$ per 0.1-Å displacement along P). The PES ($P \times R \times E$) thus obtained is shown in Figure 7. The dioxometallacycle (D in Figure 7) is in a deep potential energy well with respect to epoxide (E in Figure 7). Purcell[19] reports a similar DM (referred to as the diolate[19]) to be in a potential energy well relative to epoxide. The unfavorability of epoxide formation from the DM is easily explained in thermodynamic terms by realizing that this pathway entails the conversion of two unstrained C–O bonds (in the DM) into two strained, epoxidic C–O bonds in the product. Thus, a pathway that forms stronger C–O bonds is needed to provide any driving force. Cleavage of the C—C bond to form two C=O bonds could provide this pathway. The bond energy of a C=O bond is 190 kcal mol^{-1}.[16]

Discussion

The stated goals of the present research were to get a better understanding of the metal–dioxo/organic substrate interaction, to explore comparisons between the metal–dioxo and metal–oxo complexes, and to investigate the causes of the difference in reactivity between the *cis*- and *trans*-Ru(VI)–dioxo complexes.

The results of this research, as with our previous study of the oxidation of olefins by Ru(IV)–oxo complexes,[4b] confirm that the experimental results are easily explained in simple frontier-orbital or Woodward–Hoffmann terms. The *trans*-dioxo complex is quite similar to the monooxo complex despite the change in formal oxidation state; i.e., the most favorable pathway is a nonconcerted [1 + 2] cycloaddition to form a Ru^{IV}(O)(bound epoxide) intermediate. Both reactions can be though of as a nucleophilic attack of the olefin on the oxo oxygen. First, one C–O bond is formed, and positive charge builds up on the terminal unbound carbon, which then interacts preferentially with the electron-rich oxo to yield the bound epoxide. The lowest energy pathway for *cis*-RuO_2/olefin interaction is quite different—a [3 + 2] cycloaddition or a 1,3-dipolar addition. In the cis isomer, both oxygens are accessible to the same olefin, and thus different pathways for olefin oxidation are encouraged as a result. The DM is favored due to the stronger C–O bonds that can be made.

Finally, how can the difference in reactivity of the *cis*- and *trans*-$\text{Ru}^{VI}(\text{O})_2$ complexes be accounted for? The trans complex is more selective for epoxidations and is very stereospecific.[5b–f] The cis complex, on the other hand, leads to a large amount of cleavage products.[5a]

The larger selectivity for epoxidation pathways and high stereospecificity for the trans isomer is consistent with the most favorable pathway being the formation of the *trans*-Ru(O)(epoxide) by a nonconcerted [1 + 2] addition similar to that for Ru(IV)–oxo-catalyzed epoxidations.[4b] The small loss of stereochemistry that is observed is consistent with a process in which the formation of the second C–O bond is comparable to rotation about the C–C bond of the open structure. Formation of carbonyl products by a side reaction that entails *trans*- → *cis*-RuO_2 isomerization is not indicated. Meyer and co-workers have shown that *cis*-$\text{Os(bpy)}_2(\text{O})_2^{2+}$ is unstable with respect to the trans isomer in solution.[5d] The trans isomer is indefinitely stable in solution.[5d]

For the cis isomer, the greater amount of carbonyl product arises from the fact that conversion of the dioxometallacycle to Ru(IV)–oxo plus epoxide is a highly endothermic process. The weak epoxidic C–O bonds allow no driving force for this pathway. Any small amount of epoxide that results in the oxidation of olefins by *cis*-RuO_2^{2+} has several plausible origins. First, the higher energy *cis*-oxo/epoxide may be solvated or disproportionate before it can be converted into the DM. The calculated activation barrier of ≈6 kcal mol^{-1} might allow the *cis*-oxo/epoxide a long enough lifetime for this process to occur. Second, isomerization of the *cis*-RuO_2 complex to the trans isomer followed by epoxidation may occur. Finally, there may be present some partly oxidized Ru(IV)–oxo complex present in solution. The strengthening of the C–O single bonds in the DM to the double bonds of the cleavage carbonyl products is evidently sufficient enough to overcome the energy that must be spent in breaking the C-C bond of the DM. The well-known cleavage of O=C double bonds by RuO_4 by way of a ruthenate diester, $\overline{\text{O}_2\text{Ru–O–CH}_2\text{–CH}_2\text{–O}}$, supports this view.[20] A preliminary comparison of the decomposition pathways to bis(carbonyl) complexes for the ruthenate diester and the dioxometallacycle, using an analysis similar to that employed by Hoffmann et al. in their study of the conversion of metallocyclopentanes to bis(olefin) complexes,[21] indicates that both pathways are similar. Furthermore, both processes are allowed if one applies the simple concepts of Braterman and Cross.[22] In both the case of the cyclic diester and the case of the dioxometallacycle, the C–C σ bond correlates with a low-energy, metal-based virtual orbital of the same irreducible representation. This leads to the necessary two-electron reduction of the metal on going from the five-membered ring to the bis(carbonyl) species.

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Appendix A

$Ru(NH{=}CH{-}CH{=}NH)_2(O)_2^{2+}$ Geometry. A. Glyoxal Diimine.[14] The bond lengths and bond angles for the glyoxal diimine ligands were taken from those of bipyridine. $R(N{-}H) = 1.0$ Å; $R(C{-}H) = 1.09$ Å; $R(N{=}C) = 1.35$ Å; $R(C{-}C) = 1.50$ Å; $\theta(N{-}C{-}C) = 116.1°$.

B. Other. The Ru-N bond lengths were chosen to be the same as those found to be the equilibrium value in the INDO/1 geometry optimization of $[Ru(NH{=}CH{-}CH{=}NH)_2(NH_3)(O)]^{2+}$, i.e. ≈2.1 Å. This gives good agreement with the experimental values of 2.17-2.24 Å for Ru(VI)-dioxo complexes with nitrogen ligands reported by Che et al.[5e] The equilibrium Ru-O bond lengths were determined by varying both Ru-O bonds simultaneously (by the same amount) while the geometry of the rest of the complex was kept fixed. The equilibrium value of 1.71 Å obtained is in excellent agreement with the values of 1.71-1.72 Å obtained by Che and co-workers for Ru(VI)-dioxo complexes.[5e] $R(Ru{-}N) = 2.06$ Å; $R(Ru{=}O) = 1.71$ Å.

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, and the Arthur Amos Noyes Laboratory,[†] California Institute of Technology, Pasadena, California 91125

Luminescence from Diplatinum(III) Tetraphosphate Complexes: Dynamics of Emissive dσ* Excited States

Yeung-gyo K. Shin,[‡] Vincent M. Miskowski,[*,§] and Daniel G. Nocera[*,‡,∥]

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Solids and low-temperature solution glasses of the diplatinum(III) tetraphosphates $Pt_2(HPO_4)_4L_2^{n-}$ ($L = H_2O$, $n = 2$; L = Cl or Br, $n = 4$) exhibit red luminescence upon irradiation with near-ultraviolet light. Emission lifetimes and quantum yields of crystalline potassium salts were measured over a wide temperature range (10-300 K). Room-temperature lifetimes of 0.33, 0.71, and 0.39 μs for the axially substituted aquo, chloro, and bromo $Pt^{III}{}_2L_2$ tetraphosphates, respectively, increase dramatically with decreasing temperature. The temperature dependence of the lifetime is derived from the thermal population of a nonemissive state energetically proximate to a lowest energy emissive excited state of dσ* character (ΔE = 1126, 2256, and 2117 cm^{-1} for the $Pt^{III}{}_2(H_2O)_2$, $Pt^{III}{}_2Cl_2$, and $Pt^{III}{}_2Br_2$ tetraphosphate complexes, respectively). Temperature-dependent quantum yield measurements in conjunction with lifetime data reveal that the nonradiative decay rate constant of the upper excited state is 10^2-10^4 greater than that of the emissive excited state. Spectroscopic analysis of electronic absorption, excitation, and emission spectra is consistent with an excited-state model in which the emissive state is assigned to the $(B_{1u}(^3E_u), B_{2u}(^3E_u))$ spin-orbit component of the $^3(d\pi^*d\sigma^*)$ configuration, and the higher energy deactivating excited state is the $E_u(^3E_u)$ spin-orbit component.

Introduction

The lowest energy electronic transitions of many singly bonded metal-metal (M-M) complexes involve the population of the dσ* metal-metal level.[1-4] Typically, significant weakening of the metal-metal interaction results upon promotion of an electron to the dσ* orbital, and not surprisingly, photoinduced cleavage of the metal-metal bond has emerged as the dominant excited-state decay pathway of M-M species.[5-16] The d^7-d^7 dimer $Mn_2(CO)_{10}$ is the cornerstone example of such a photochemical process. Excitation into the dimer's absorption manifold, which is dominated by the intense dσ-dσ* absorption band and weaker dπ-dσ* band to lower energy,[17] leads to cleavage of the Mn-Mn bond to yield neutral $^\bullet Mn(CO)_5$ radical fragments.[18-24] Because dσ* deactivation pathways are extremely efficient, the lifetimes of electronically excited M-M complexes are short,[25] and luminescence from M-M complexes is rare. To this end, coordination of M-M cores by bridging ligands will prevent metal-metal dissociation and the expectation of luminescence from M-M complexes is a reasonable one. Indeed recent observations of luminescence from diplatinum(III) pyrophosphite complexes, $Pt_2(pop)_4X_2^{4-}$ (pop = $(HO_2P)_2O$, X = halide),[26] a binuclear dirhodium(II,0) fluorophosphine complex, $Rh_2[(F_2P)_2N(CH_3)]_3(PF_3)Cl_2$,[27] and bidentate phosphine derivatives of $Re_2(CO)_{10}$[28] represent the first examples of dσ* luminescence. These complexes contain bridging ligands with only one bridgehead atom, and thus, deactivation by metal-metal bond cleavage in the excited state is circumvented. However, although retention of the M-M core in the excited state is a necessary condition of dσ* luminescence, it is not sufficient. The paucity of emissive M-M complexes despite the synthesis of several bridged complexes during the past years suggests that subtler, less well understood perturbations play an important role in the deactivation of dσ* excited states.

[†] Contribution No. 7927.

[‡] Michigan State University.

[§] California Institute of Technology.

[∥] Alfred P. Sloan Fellow and Presidential Young Investigator.

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