Lewis Acidity and Reactivity of Transition Metal Oxo Complexes. A Comparative Density Functional Study of CH_3ReO_3, CH_3TcO_3, and Their Base Adducts

Sibylle Köstlmeier,[†] Vladimir A. Nasluzov,[†] Wolfgang A. Herrmann,[‡] and Notker Rösch*,[†]

Lehrstuhl für Theoretische Chemie, Technische Universität München, 85747 Garching, Germany, and Anorganisch-Chemisches Institut, Technische Universität München, 85747 Garching, Germany

Received September 30, 1996[⊗]

A density functional investigation of methyltrioxo−rhenium and its lower homologue methyltrioxo−technetium studying the influence of relativistic effects on the reactivity of the two metal centers is presented. In order to quantify the Lewis acidity of the central metal atom, the adduct formation with NH_3 as a probe molecule is investigated. Methyltrioxo−rhenium is calculated to form a stable base adduct at a Re−N distance of 2.50 Å (exp 2.40−2.50 Å). The calculations for the Tc complex (and for the Re complex at a nonrelativistic level of theory) yield longer M−N distances (by 0.1 Å) and lower stretching frequencies for the M−N bond in line with the fairly small association energies. From the calculated NH_3 adduct formation energies supported by an analysis of the charge distribution, one concludes that Re is a somewhat stronger Lewis acid center than Tc in the MO_3 moiety. The polarizability (hardness) of the MO_3 fragment is quantified by the HOMO−LUMO splitting as well as by the M−O displacement derivatives of the partial charges and of the dipole moment. These criteria indicate that the reactive MO_3 site of methyltrioxo−rhenium, a model for other electron-deficient early transition metal oxo compounds, is less polarizable and thus will react preferentially with a hard Lewis base such as NH_3 to adducts or with H_2O_2 to the catalytically active peroxo species. The softer Lewis acidic technetium analogue shows a polarizability similar to that of OsO_4 or of late transition metal complexes and thereby is able to directly attack soft Lewis bases, such as olefins. In this way, the fundamental reactivity differences of methyltrioxo−rhenium and osmium tetraoxide can be rationalized.

Introduction

An important goal of theoretical investigations in catalysis is to explore measures that can be provided by theoreticians to characterize catalytically active species with regard to their chemoselectivity. In the study presented here, special emphasis is put on the role the electronic structure of the catalyst plays in this context; steric factors of influence shall be excluded for purpose of simplicity. Thus, we chose molecular metal oxides that catalyze olefin oxidation as model systems, since a large variety of chemoselectivities can be found although the structure of the catalysts differ only on a limited scale. Two prominent examples are methyltrioxo−rhenium and its lighter homologue methyltrioxo−technetium, since they are virtually isostructural, but exhibit different chemoselectivities in olefin oxidation.

Methyltrioxo−rhenium (CH_3ReO_3) and its derivatives are known as powerful oxidizing agents for olefin epoxidation.[1,2] The catalytically active species has been experimentally characterized as a methyloxo−(bisperoxo)−rhenium(VII) complex, which is formed upon addition of H_2O_2 to methyltrioxo−rhenium.[3] This type of oxidation reaction is also mediated by a number of other early transition metal complexes; several hypotheses have been advanced on the nature of the active species, on the mechanism of the olefin attack, and on the epoxide extrusion from the intermediate or the transition state.[4−7] Common to all of them is the feature that in the first step the metal oxo complex is activated by the oxidant to the peroxo species rather than directly attacked by the olefin.

In the case of methyltrioxo−technetium, no peroxo species could be detected and it is assumed that the olefin reacts directly with the oxo complex to give an intermediate of ester-type structure. Solvolysis cleaves this cyclic ester, and diols result as oxidation products instead of epoxides.[8] Several theoretical and experimental investigations have been carried out on OsO_4, aiming at the elucidation of the reactive mechanism.[9,10] Based on experimental and theoretical evidence the

---

* Author to whom correspondence should be addressed.

[†] Lehrstuhl für Theoretische Chemie.

[‡] Anorganisch-chemisches Institut.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

(1) Herrmann, W. A. *J. Organomet. Chem.* **1995**, *500*, 149, and references within.

(2) Al-Ajlouni, A. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 9243.

(3) Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. U. *Angew. Chem., Int. Ed. Engl.* **1993**, *30*, 1638.

(4) Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *22*, 734.

(5) Mimoun, H. *Catal. Today* **1987**, *1*, 281.

(6) Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 295.

(7) Thiel, W.; Angstl, M.; Hansen, N. *J. Mol. Catal. A* **1995**, *103*, 5.

(8) Herrmann, W. A.; Alberto, R.; Kiprof, P.; Baumgärtner, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 189.

(9) Veldkamp, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 4937.

S0276-7333(96)00831-X CCC: $14.00

plausible reaction pathway involves a two-step mechanism via a cycloaddition and a subsequent cycloreversion, starting with a nucleophilic attack of an Os=O bond or the O=Os=O moiety by an olefin. This implies that in the case of OsO_4, and probably also for CH_3TcO_3, the direct reaction with the olefin is preferred over the one with H_2O_2.

As pointed out above, there are strong indications that the two compounds CH_3TcO_3 and CH_3ReO_3 are isostructural. Although there is so far no X-ray study of the structure of CH_3TcO_3, a comparison of the dimerization product $[(CH_3)_2TcO_2]_2$ to the analogous Re dimer provides convincing evidence that the related Tc and Re monomers have in fact the same structure.[8] Steric effects should be of equal magnitude for both molecules $[CH_3MO_3]$ (M = Tc, Re), and therefore, these compounds constitute an ideal model system to work out the electronic factors relevant to their different reactivity. In order to elucidate the role of relativistic effects, some nonrelativistic density functional calculations were performed for CH_3TcO_3 and CH_3ReO_3 in addition to the scalar relativistic ones. The resulting four model systems will be denoted as CH_3TcO_3 (nrel + rel) and CH_3ReO_3 (nrel + rel) in the following.

From Dirac−Fock calculations it is known[11] that the effective radius of the Re atom as measured by the radial expectation value of the valence shell is smaller than the one of Tc due to the relativistic contraction of the s shells. Re can thus be considered the more compact and less polarizable atom. Assuming the same arguments to hold for ionic states of Tc and Re, it can indirectly be concluded that in isostructural compounds a Re center should be the stronger and harder Lewis acidic site within the molecular framework. This property can be directly quantified by studying the corresponding base adducts with a hard Lewis base such as NH_3. An analysis of some fundamental properties of the $CH_3MO_3{\cdot}NH_3$ adducts (M = Tc, Re), such as binding energies, bond distances, and harmonic stretching frequencies, provides further insight into the factors that may influence the first step of the various catalytic cycles.

Computational Details

All-electron molecular orbital calculations were carried out using the linear combination of Gaussian-type orbitals density functional (LCGTO-DF) method[12] to solve the effective one-electron equations which result in the Kohn-Sham approach to density functional theory. With the help of the scalar relativistic variant of the program[13] we were able to self-consistently include relativistic effects (mass−velocity and Darwin term) in the electronic structure calculations. This scalar relativistic method has already been successfully utilized for investigating a variety of compounds containing heavy elements.[14−17] For the exchange correlation energy functional, a generalized gradient approximation[18,19] was used; the corresponding terms were evaluated numerically and included self-consistently in the Kohn−Sham procedure.[20] The binding energies of the adducts $CH_3MO_3{\cdot}NH_3$ were found to be essentially free of the basis set superposition error; for both metals, Tc and Re, this error was estimated to −0.02 eV (rel) and −0.03 eV (nrel) by calculating both fragments in the whole basis (counterpoise technique).[21] Partial (atomic) charges were characterized with the help of a Mulliken analysis.

For Re, the initial (19/14/10/5) molecular orbital basis set[22] was augmented to (21/17/12/7) and contracted to [9/8/5/2] as described previously.[23] The osmium basis set was constructed in analogous fashion; the initial (19/14/10/5) basis[22] was supplemented by two s exponents (0.013 21, 0.033 30), three p exponents (0.024 74, 0.061 85, 0.154 635), two d exponents (0.047 486, 0.118 714), and one f exponent (0.368 41) and was finally contracted to [9/8/5/2]. The basis for technetium was taken from the same source,[22] augmented to (18/13/8) by addition of one s exponent (0.27019) and one p exponent (0.09466), and contracted to [8/7/4]. For C and N, a (9/5/1) basis set was contracted to [7/4/1]; for H, the basis set was (6/1) → [4/1].[24] For oxygen, a basis set of type (11/7)[25] was augmented by a d polarization exponent (1.154) and contracted to [6/4/1]. All contractions were of the generalized form based on eigenvectors of the corresponding atomic calculations. The exponents of the polarization functions, d-type for C, N, and O and p-type for H, were taken from ref 26. The fitting basis sets used to represent the electron charge density have been generated in a standard fashion.[12]

Using a recently developed extension of the LCGTO-DF program, full geometry optimizations were carried out on all the structures (under the constraint of C_{3v} symmetry) employing analytical gradients of the total energy.[20] The stretching frequencies of the M−N bond in the NH_3 adduct complexes were calculated by changing the M−N distance of the minimum energy structures in increments of ±10 and ±20 pm without subsequent geometry relaxation and by interpolating the resulting energy curve.

Several theoretical concepts have been presented in the literature for quantifying the hardness η of an electronic system.[27] A common procedure derives a value for η from the difference between the first ionization potential and the electronegativity of a system.[28] Other measures, as for instance the Fukui function[29] or a Clapeyron equation for charge transfer processes along a reaction coordinate,[30] allow for an atom-resolved characterization of a compound with respect to electrophilic or nucleophilic and hard or soft centers of reactivity within the molecule. In the framework of density functional theory, as employed in the present study, one may approximate[27] the hardness η as half the absolute value of the HOMO−LUMO splitting, since this property can eventually be related to experimental values on the corresponding ionization potential and the electron affinity.

Results and Discussion

Geometric and Electronic Structure of CH_3TcO_3 and CH_3ReO_3. Elements of the second and third

---

(10) Norrby, P.-O.; Kolb, H. C.; Sharpless, K. B. *J. Am. Chem. Soc.* **1994**, *116*, 8470.

(11) Desclaux, J. P. *At. Data Nucl. Data Tables* **1973**, *12*, 311.

(12) Dunlap, B. I.; Rösch, N. *Adv. Quantum Chem.* **1990**, *21*, 317.

(13) Häberlen, O. D.; Rösch, N. *Chem. Phys. Lett.* **1992**, *199*, 491.

(14) Rösch, N.; Häberlen, O. D.; Dunlap, B. I. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 108.

(15) Häberlen, O. D.; Schmidbaur, H.; Rösch, N. *J. Am. Chem. Soc.* **1994**, *116*, 8241.

(16) Chung, S.-C.; Krüger, S.; Pacchioni, G.; Rösch, N. *J. Chem. Phys.* **1995**, *102*, 3695.

(17) Rösch, N.; Krüger, S.; Mayer, M.; Nasluzov, V. A. In *Recent Developments And Applications Of Modern Density Functional Theory*; Seminario, J. M., Ed.; Elsevier: Amsterdam, 1996; p 497.

(18) Becke, A. D. *Phys. Rev. B* **1988**, *42*, 1088.

(19) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(20) Nasluzov, V. A.; Rösch, N. *Chem. Phys.* **1996**, *210*, 413.

(21) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(22) Gropen, O. *J. Comput. Chem.* **1987**, *8*, 782.

(23) Köstlmeier, S.; Häberlen, O. D.; Rösch, N.; Herrmann, W. A.; Solouki, B.; Bock, H. *Organometallics* **1996**, *15*, 1872.

(24) van Duijeneveldt, F. B. *IBM Res. Rep.* **1971**, *945*.

(25) Pacchioni, G.; Cogliandro, G.; Bagus, P. S. *Int. J. Quant. Chem.* **1992**, *42*, 1115.

(26) Huzinaga, S., Ed. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: New York, 1984.

(27) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(28) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734.

(29) Parr, R. G. *Int. J. Quantum Chem.* **1984**, *26*, 687.

(30) Berkowitz, M. *J. Am. Chem. Soc.* **1987**, *109*, 4823.

Table 1. Relativistic Effects on Observable Quantities of CH_3MO_3 (M = Tc, Re)[a]

	CH_3ReO_3			CH_3TcO_3	
	exp[b]	rel	nrel	rel	nrel
r(M−C)	2.06	2.08	2.13	2.09	2.11
r(M−O)	1.71	1.72	1.76	1.72	1.72
∠(CMO)	106	105	105	105	105
∠(OMO)	113	113	114	114	114
μ	2.6	2.89	2.73	2.69	2.64
$E_b(CH_3)$[c]		4.59	4.06	4.03	3.84

[a] Comparison of nonrelativistic (nrel) and relativistic (rel) DF results with experimental data (CD_3ReO_3) on bond lengths (in Å), bond angles ∠ (in deg) and dipole moments μ (oriented along the M−C bond, in D). [b] Reference 1. [c] Energy of the M−C bond (in eV). $E_b(CH_3) = E(CH_3) + E(MO_3) - E(CH_3MO_3)$.

transition metal series have virtually the same effective atomic or ionic radii, thus, complexes employing the same ligand shell are found to have essentially the same structure.[8,31] In part this similarity of the molecular geometries is due to the so-called lanthanide contraction, which refers to the fact that in third-row transition metals the 4f shell is rather compact and can be considered as corelike (e.g., for Re core: 4p 0.25 au, 4d 0.26 au, 4f 0.31 au; valence: 5d 1.02 au, 6s 1.62 au).[11] Therefore, the 4f shell effectively shields the increased nuclear charge in heavy elements and the radial expectation values of the valence shell become nearly equal in the second and the third transition metal row.[11] Additionally, on dealing with heavy elements such as rhenium, a further contraction of the s shells due to the relativistic mass increase of electrons in the near core region has been calculated.[11] Technetium, on the other hand, belongs to the borderline elements of the second transition series and the relativistic contraction of the Tc s shells has been found to be below 4%.[11] Hence, if both CH_3ReO_3 and CH_3TcO_3 are treated including relativistic effects, virtually the same geometrical structure is obtained for the two compounds, whereas the contraction of the Re s shells leads to differences in the electronic structure.

Table 1 provides details on the calculated geometries for CH_3ReO_3 and CH_3TcO_3, both for the scalar relativistic and for the nonrelativistic methodology, and compares them to the results of an experimental powder diffraction study of CD_3ReO_3.[1] As far as the bond angles are concerned, experimental and theoretical results (rel + nrel) are in excellent agreement, since the relativistic effect to be studied is mainly of radial nature. A comparison of the bond lengths shows differences between relativistic and nonrelativistic treatments: in the relativistic case, only minor deviations from experiment are found, amounting to 0.02 Å at the utmost for the σ(Re−C) bond, which turns out to be the most sensitive one toward the level of theory employed (+0.03 Å for σ(Tc−C) compared to experiment[1]). With r(M−O) = 1.72 Å and r(C−H) = 1.10 Å, all other bonds are of equal length in both molecules and in excellent agreement with the experimental structure data on CD_3ReO_3.[1] In a nonrelativistic treatment, the agreement with experimental data is diminished markedly for the Re−C bond, which is lengthened by 0.05 Å and becomes considerably too long with respect to the powder diffraction data.[1] The Re−O bonds exhibit more metal d character than the Re−C bond; hence they are not directly affected by the contraction of the Re s shells and the relativistic contraction is less pronounced. For the technetium analogue, some minor relativistic effect is observed for the Tc−C bond, only.

The valence MO spectrum of CH_3ReO_3 has been discussed in detail elsewhere;[23] we comment here only on features of relevance in the present context. From the discussion of the geometrical data one may conclude that the influence of relativistic effects on the electronic structure is best monitored by the M−C bonding molecular orbital (MO). Indeed, the σ(M−C) bonding MO of CH_3ReO_3 (nrel) is considerably upward shifted, by ~0.9 eV, relative to CH_3ReO_3 (rel) due to the destabilization of the Re 6s orbital. In the relativistic case, this 6s orbital contributes to the σ(M−C) MO by 17%, whereas in CH_3TcO_3 (rel + nrel) and CH_3ReO_3 (nrel), the 5s participation is only 10% or lower. From calculations on the neutral fragments CH_3 and MO_3, the relativistic stabilization of the M−C bond amounts to ~0.5 eV for CH_3ReO_3, but only 0.2 eV for the Tc analogue (Table 1). The stronger bonding of CH_3 to MO_3 in the Re case (Table 1) correlates with observations on the stability: CH_3ReO_3 is observed to be stable in water whereas from CH_3TcO_3 polymeric technetium oxides are formed under irreversible cleavage of the Tc−C bond, if the compound is exposed to moisture.[8]

Geometric and Electronic Structure of the Base Adducts $CH_3TcO_3{\cdot}NH_3$ and $CH_3ReO_3{\cdot}NH_3$. The role of base adduct formation has been experimentally studied both for epoxidation catalysts such as $L^1L^2MoO(O_2)_2$[4,7,32] and for cis-dihydroxylating agents like OsO_4 and its derivatives.[9,10,33] In the latter system, mostly steric effects have been discussed in an attempt to explain the enantiomeric selectivity in the cis-dihydroxylation of olefins mediated by bulky chiral base ligands.[10] Several theoretical studies have been devoted to the electronic effects of donor base ligands on the central metal, mostly at a semiempirical level.[34−36] A study on the MO_3 fragment (M = Tc, Re) in dinuclear clusters has been reported, investigating the acceptor properties of this moiety in the vicinity of another transition metal atom.[37] Here, a description of the basic features of the model adducts $CH_3MO_3{\cdot}NH_3$ (M = Tc, Re) shall be given along with a discussion of relativistic effects on this type of dative bond.

There is experimental evidence that the interaction of some labile alkyl compounds $RReO_3$ with a donor base L leads to a pronounced stabilization.[38,39] In line with these findings, it has also been observed that the catalytic activity, but not the selectivity of complexes $RReO_3$ with respect to olefin epoxidation, is reduced upon base adduct formation.[40] This may in part be due

---

[31] Jørgensen, K. A. *Chem. Rev.* **1989**, *89*, 431.

[32] Mimoun, H.; de Roch, I. S.; Sajus, L. *Tetrahedron* **1970**, *26*, 37.

[33] Herrmann, W. A.; Eder, S. J.; Kiprof, P.; Rypdal, K.; Watzlowik, P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1447.

[34] Purcell, K. F. *Organometallics* **1984**, *4*, 509.

[35] Jørgensen, K. A.; Hoffmann, R. *Acta Chem. Scand.* **1986**, *B40*, 411.

[36] Filatov, M. J.; Shalyaev, K. V.; Talsi, E. P. *J. Mol. Catal.* **1994**, *87*, L5.

[37] Costas, M.; Poblet, J. M.; Rohmer, M. M.; Bénard, M. *Inorg. Chem.* **1995**, *34*, 176.

[38] Herrmann, W. A.; Kühn, F. E.; Romão, C. C.; Huy, H. T.; Wang, M.; Fischer, R. W.; Kiprof, P.; Scherer, W. *Chem. Ber.* **1993**, *126*, 45.

[39] Herrmann, W. A.; Romão, C. C.; Fischer, R. W.; Kiprof, P.; de Méric de Bellefon, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 185.

[40] Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *J. Mol. Catal.* **1994**, *86*, 243.

Table 2. Characteristic Properties of the Base Adducts of CH_3MO_3 (M = Tc, Re) with NH_3[a]

	CH_3ReO_3		CH_3TcO_3	
	rel	nrel	rel	nrel
r(M−C)	2.10	2.14	2.11	2.12
r(M−O)	1.73	1.76	1.73	1.74
r(M−N)	2.51	2.57	2.58	2.60
∠(CMO)	98	98	98	98
∠(OMO)	118	118	118	118
$E_b(NH_3)$	0.48	0.29	0.27	0.26
ν(M−N)	302	254	219	220
k(M−N)	0.79	0.60	0.37	0.43
Δ(C)	+1.10	+1.04	+1.03	+1.03
Δ(O)	+0.90	+0.78	+0.79	+0.76
Δ(N)	−1.83	−1.72	−1.57	−1.55

[a] Comparison of nonrelativistic (nrel) and scalar relativistic (rel) DF results on bond lengths r (in Å), bond angles ∠ (in deg), binding energies $E_b(NH_3)$ ($E_b(NH_3) = E(NH_3) + E(CH_3MO_3) - E(CH_3MO_3 \cdot NH_3)$) (in eV), vibrational frequencies ν (in cm^{-1}), and force constants k (in mdyn/Å). Also shown are the 1s core level shifts Δ of the atoms C, O, and N calculated as the differences between the Kohn−Sham level energies (in eV) of the separate fragment (NH_3 or CH_3MO_3) and of the adduct.

to increased steric crowding at the metal center; yet, the electronic effect of the metal−donor interaction should also influence the other ligands to some extent. On the other hand, base adduct formation has not been observed for trioxo−technetium complexes. Hence, a study of the electronic properties of the adduct $L \cdot CH_3MO_3$ (M = Tc, Re) can provide further insight into the possibilities of reaction control by fine-tuning the ligand shell.

The changes to the CH_3MO_3 (M = Rc, Re) molecules and to the free NH_3 donor base upon adduct formation can be discussed in terms of geometrical parameters (for C_{3v} symmetry), such as bond lengths and angles, and of vibrational data of the four different adduct systems under investigation: $CH_3ReO_3 \cdot NH_3$ and $CH_3TcO_3 \cdot NH_3$ (rel + nrel each). Throughout the series, no pronounced bond length changes within the adducts with respect to the free fragments are obtained from the DF calculations. The influence of relativistic effects on bonds that employ MOs with high metal s character results in the same characteristics as in the corresponding "free" system CH_3MO_3 (M = Tc, Re). On formation of the adduct, a trend to slightly elongated bonds become discernible (cf. Tables 1 and 2); thus, the changes may indicate some weakening of the metal-to-ligand interaction. Yet, the bond length increments, up to +0.02 Å, are rather small and therefore will not be interpreted any further. Compared to experimental data on several base adducts,[41] very good agreement is obtained: r(Re−C) = 2.09 Å exp, 2.10 Å calc; r(Re−O) = 1.71 Å exp, 1.73 Å calc for CH_3ReO_3 (rel). All values given refer to the eclipsed arrangement of the ammonia hydrogens and the oxygen centers (Figure 2). A slight preference for this geometry is obtained (0.05 eV), probably due to a Coulomb attraction between the partially positive hydrogen centers of NH_3 and the negative oxygen centers of the ReO_3 moiety. Also, in the experimentally determined X-ray structures of some CH_3ReO_3 base adducts, a propensity for closer contacts between the ReO_3 oxygen atoms and the hydrogens of the Lewis base can be deduced.[41]

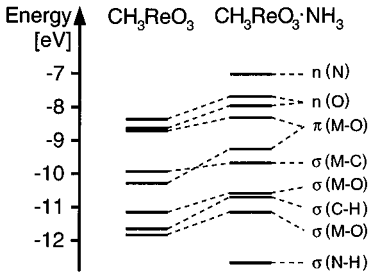

Figure 1. Changes to the valence MO energy spectrum of CH_3ReO_3 upon adduct formation with NH_3 from a relativistic DF calculation.

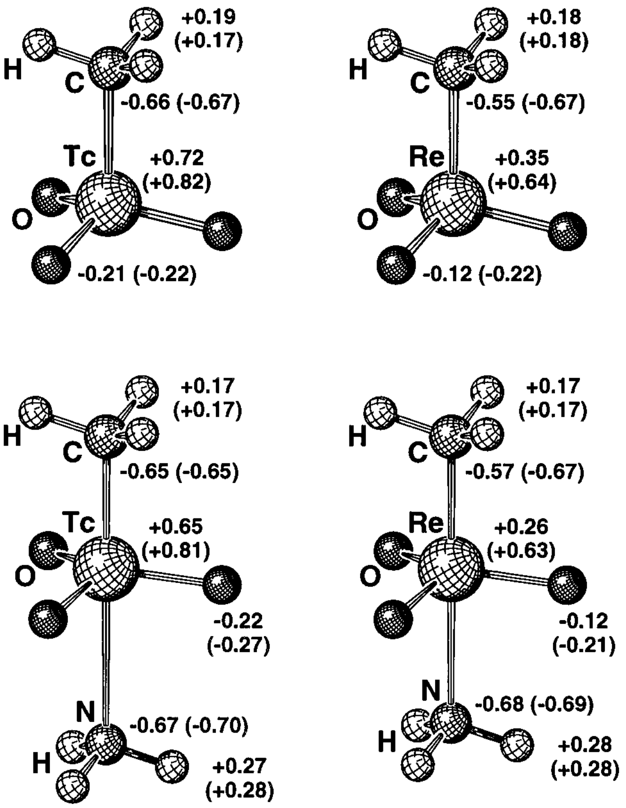

Figure 2. Structures and partial charges (in au) from a Mulliken analysis for CH_3MO_3 (M = Tc, Re). The charge values from nonrelativistic calculations are given in parentheses; the structures were drawn employing the program SCHAKAL.[44]

The bond angles are calculated to vary on transition from the pseudotetrahedral arrangement at the metal center in CH_3MO_3 to the nearly trigonal-bipyramidal structure of the NH_3 adduct. The angle ∠(OMO) opens up from 113−114 to ~118° so that the MOs fragment is almost planar in all models, irrespective of some minor differences in the free fragments. For the other characteristic angle, ∠(CMO), values of 98° are obtained in all four systems, reduced relative to 105° in the free molecules CH_3MO_3, but the oxygen atoms of the ReO_3 fragment are still directed toward the base. Experimentally, the same planarization of the ReO_3 fragment has been measured, and the angles (∠(OMO) = 119°; ∠(CMO) = 97°)[1] are reproduced very well by the calculations. The addition of the base ligand and the subsequent geometry changes provide already one reason for the reduced reactivity of CH_3ReO_3 base adducts in olefin epoxidation chemistry, as with an

---

(41) Herrmann, W. A.; Weichselbaumer, G.; Herdtweck, E. *J. Organomet. Chem.* **1989**, *372*, 371.

increased number of ligands the molecule becomes more sterically crowded around the metal.

Some attention should be drawn to the length of the dative M−N bond. With a value of 2.51 Å, it is calculated shortest in the case of CH_3ReO_3 (rel), whereas the other three model systems, CH_3ReO_3 (nrel) and CH_3TcO_3 (rel + nrel) exhibit a rather shallow minimum on the energy surface at larger distances of 2.57−2.60 Å. All these values are considerably longer than the typical Re−N distance measured for a single bond, r(Re−N) = 2.10 Å; thus the adduct bond is very weak (see below).[1] M···N distances typical for dative bonds have been experimentally determined to 2.41 Å in the CH_3ReO_3 quinuclidine adducts[41] and to ~2.46 Å for toluidine and aniline adducts.[42] The calculated bond length for $CH_3ReO_3{\cdot}NH_3$ is somewhat longer, r(Re−N) = 2.51 Å, and therefore one expects that the base−metal interaction is slightly underestimated compared to experiment. The model character of NH_3 as a substitute for the bases employed in experiment may affect this bond distance. In line with these results, the metal−base interaction is smaller for CH_3TcO_3, in accordance with the experimental observation that CH_3TcO_3 base adducts are hitherto unknown. This trend is confirmed by a calculation of the corresponding NH_3 binding energies. In the case of CH_3ReO_3 (rel), a value E_b = 0.46 eV is calculated, noticeably larger than the binding energies obtained for the three other models, which are lower than 0.3 eV.

Finally, the calculated stretching frequencies of the M−N bond confirm this picture. The M−N force constant of CH_3ReO_3 (rel) is calculated about twice as large as for CH_3TcO_3 (nrel + rel). The corresponding M−N stretching mode is determined highest in CH_3ReO_3 (rel); its value is by more than 50 cm^{-1} larger compared to the other models and therefore is already in the region of the torsional motion of the CH_3 moiety and other skeletal distortion vibrations.[23] The difference in force constants mirrors the enhanced stability of the $CH_3ReO_3{\cdot}NH_3$ adducts compared to the corresponding Tc compounds and also depicts the stabilization of $CH_3ReO_3{\cdot}NH_3$ due to relativistic effects. From all calculated results one concludes that relativistic effects have no influence on the reactivity of CH_3TcO_3 and that CH_3ReO_3 (nrel) bears a high resemblance to its Tc congener.

In order to gain some insight into the changes to the electronic structure that are induced by base adduct formation, the Kohn−Sham orbital energy spectrum of CH_3ReO_3 (rel) shall be analyzed briefly. On adduct formation with NH_3, all valence levels of CH_3ReO_3 (rel) are shifted upward, i.e., toward lower electron binding energies, on the average by 0.65 eV (Figure 1). Two factors induce this shift: first, the Pauli repulsion between the ReO_3 moiety and the lone pair of the ammonia N center and, second, the charge transfer from the donor base to the Lewis acidic central metal and further on into the ligand sphere.

Concomitantly, the MOs of the NH_3 fragment are shifted to higher binding energies relative to the values calculated for the free molecule. The stabilization of the lone pair n(N) becomes rather prominent with a downward shift of 0.92 eV, and the σ(N−H) bonding MO is even shifted down by 1.68 eV. This modification to the electronic structure of free NH_3 is easily reproduced by a model calculation on the partially positivated "free" base. In order to reproduce the energy shift of the lone pair, a partial "ionization" by +0.1 au is required; similarly, to obtain the correct shift of the σ(N−H) bond, the necessary effective charge on NH_3 must be ~0.2 au. From these findings it becomes obvious that rather small amounts of electron transfer are able to considerably influence the electronic structure of the system and to eventually cause noticeable modifications of the molecule's reactivity.

Lewis Acidity and Reactivity of Transition Metal Oxo Complexes. The present comparison of CH_3ReO_3 and CH_3TcO_3 provides a unique starting point for a more general investigation into the factors that make any transition metal oxo complex either an epoxidation or a hydroxylation catalyst. According to the majority of experimental observations,[31] the borderline between these two regimes can be drawn between the element pairs V/Cr, Mo/Tc, and Re/Os, i.e., diagonally in the periodic table as it is common for properties that are determined by the effective charge, radius, and polarizability of an atom or ion. To investigate the interplay of these properties further, the study will be extended to OsO_4 in the following. This compound compares well to the two models CH_3MO_3 (M = Tc, Re) because of its tetrahedral geometry, which resembles the pseudotetrahedral structures discussed above (r(Os−O) = 1.70 calc, 1.71 exp[43]). OsO_4 is also the compound of choice, as it is a far more common dihydroxylating agent than CH_3TcO_3.

(1) Charge Distribution. Electronegativity. To gain some insight into the charge distribution within the molecules, we have calculated measures that allow for an atom-resolved analysis of the charge distribution and monitor the changes induced by the base adduct formation.

First we will briefly discuss the shifts of the calculated 1s core levels of the atoms C, N, and O due to formation of the base adduct (Table 2). Positive shifts, indicating an electronic charge transfer to the corresponding atom, are found for all centers of the CH_3MO_3 fragment, especially for carbon, which experiences the most pronounced shifts of up to +1.10 eV. Concomitantly, the N 1s core level of all four models $CH_3MO_3{\cdot}NH_3$ is downward shifted, indicating loss of electronic charge on the NH_3 fragment, especially if M = Re.

Another measure for the charge redistribution is provided by the comparison of the Mulliken population analysis for the free fragments and the adducts. The results are displayed[44] in Figure 2 along with the adduct structures optimized at a relativistic level of theory; values for the Mulliken charges from nonrelativistic treatment are listed in parentheses.

Comparing the free CH_3MO_3 molecules, the similarity of the electronic charge distribution of the technetium system (nrel + rel) and CH_3ReO_3 (nrel) is obvious: corresponding partial charges are quite close. In these three model systems, the metal charge varies by q(M) = +0.72 ± 0.10 au, and there is a pronounced difference

---

(42) Herrmann, W. A.; Correia, J. D. G.; Kühn, F. E.; Artus, G. R. J.; Romão, C. C. *Chem. Eur. J.* **1996**, *2*, 168.

(43) Herzberg, G. *Molecular Spectra and Molecular Structure, III. Electronic Spectra Electronic Structure of Polyatomic Molecules*; Van Nostrand: New York, 1966.

(44) Keller, E. *SCHAKAL 92*, Kristallographisches Institut der Universität Freiburg, Germany, 1992.

to CH_3ReO_3 (rel), $q(Re) = +0.35$ au. At first glance this rather low partial charge of Re seems to contradict the fact that Re(VII) (rel) displays a higher affinity toward the NH_3 lone pair than Tc(VII), a fact expected to correlate with a larger positive charge on Re. Yet, the Re center is surrounded by doubly bonded oxygen atoms, and because of its high electronegativity, it is able to withdraw more electronic charge from these centers than Tc in the corresponding compound.

When NH_3 is added, the partial charges of the metals in all model systems decrease due to the charge donation from the NH_3 molecule ($\Delta q(Re) = -0.09$, $\Delta q(Tc) = -0.07$ in the relativistic case). The Re (nrel) NH_3 adduct closely resembles the corresponding Tc compound. In conjunction with the calculated NH_3 adduct formation energies (see above) these findings may be taken as an indicator that Re is a somewhat stronger Lewis acid center than Tc in the MO_3 moiety.

The experimentally observed deactivation of methyltrioxo−rhenium by base adduct formation may thus be affected not only by steric but also by electronic factors: the strength of the Lewis acidic site is diminished due to charge transfer via the dative bond.

(2) Polarizability. Hardness. So far, the discussion of electronic properties has been focusing only on the strength of a Lewis acid, a quantity that is directly related to the electronegativity χ of an atom or a fragment and that determines its reactivity. Apart from this property, the character of a Lewis acid with respect to the classification in terms of "hard" and "soft" according to the concept of hard and soft acids and bases ("HSAB" concept)[45] is of importance for a deeper understanding of chemical selectivity. The hardness of an atomic center has been correlated to its polarizability:[27,45,46] the more localized and less polarizable an electronic charge distribution, the harder the acid or base. Hard reagents are characterized by a large energy gap between the highest occupied and the lowest unoccupied MO, which implies that polarization effects become negligible and the main interaction between two hard reaction partners is of Coulomb type. The reactivity of soft acids and bases, on the other hand, is based on more covalent interactions between the two fragments. As discussed in Computational Details, we use here half the HOMO−LUMO splitting to quantify the hardness η of a system.[27]

By far the largest value for η, 2.22 eV, is calculated for free CH_3ReO_3 (rel), whereas all other model systems exhibit values below 2 eV (Table 3): 1.97 eV for CH_3ReO_3 (nrel), 1.84 eV for CH_3TcO_3 (rel), and 1.77 eV for CH_3ReO_3 (nrel). OsO_4 (rel) compares best to CH_3ReO_3 (nrel) ($\eta = 1.96$ eV), whereas OsO_4 (nrel) is calculated to be the softest acid with $\eta = 1.70$ eV. As Os belongs to the third transition metal row, the difference between the results of the relativistic and the nonrelativistic calculation is as large as for the Re compound; hence the value of η for OsO_4 (rel) should be chosen for further interpretation of experimental findings. Despite the large formal charge of +VIII at Os, the hardness of OsO_4 comes closer to the one of CH_3TcO_3; thus the polarizability (softness) of the oxidizing agents increases as $CH_3ReO_3 < OsO_4 < CH_3TcO_3$.

Adduct formation with NH_3 ($\eta = 3.28$ eV) lowers the overall η values by 0.4−0.5 eV (Table 3) and the differences between $CH_3ReO_3 \cdot NH_3$ (rel) and the other systems under investigation become larger. Focusing on the change in η for CH_3ReO_3 (rel), one concludes that the base-induced polarizability change is small compared to the other models and thus the rather strong interaction between CH_3ReO_3 (rel) and NH_3 is more of electrostatic nature. However, the absolute hardness of CH_3ReO_3 (rel) drops to a value comparable to free CH_3TcO_3 (rel), providing yet another argument why base adducts of this compound have been observed to be catalytically less active.

Table 3. Hardness η from the HOMO−LUMO Splitting (in eV) of OsO_4, CH_3MO_3 (M = Tc, Re), and the NH_3 Adducts as Well as the Corresponding Difference $\Delta\eta$, Calculated by the Relativistic (rel) and Nonrelativistic (nrel) Variant of the DF Method

	Re		Tc		Os	
	rel	nrel	rel	nrel	rel	nrel
η(free)	2.22	1.97	1.84	1.77	1.96	1.70
η(adduct)	1.83	1.51	1.37	1.26		
$\Delta\eta$	0.39	0.46	0.48	0.51		

Table 4. Polarizability of the M−O Bond in CH_3MO_3 (M = Tc, Re) and OsO_4 from Relativistic DF Calculations[a]

	Re	Tc	Os[b]
$\partial q(M)/\partial r$	−0.00	−0.18	−0.60
$\partial q(O)/\partial r$	−0.01	+0.06	+0.15
$\partial q(C)/\partial r$	−0.01	−0.00	
$\partial \mu/\partial r$	−0.69	−0.77	−0.80

[a] Given are the derivatives of the Mulliken partial charges q on the centers M, O, and C and of the total dipole moment μ (oriented along the M−C bond) with respect to the M−O distance r for a simultaneous elongation of three M=O bonds (C_{3v} symmetry). All quantities in au. [b] One Os−O bond kept fixed.

Following a strategy for resolving the hardness with respect to atomic centers within a molecule,[30] the M−O bonds (only three bonds of OsO_4) have been simultaneously elongated from their optimized values in steps of 0.05 Å, i.e., retaining C_{3v} symmetry. This crude model for M−O bond lengths changes occurring along possible reaction pathways may provide more detailed information on the role polarizability plays in the reactive MO_3 fragments. The charge redistribution within the molecule is monitored by the derivative of the Mulliken partial charges on M, O, and C with respect to the M−O bond stretch (Table 4). Within a displacement range of 0.25 Å, the changes of the partial charges in CH_3ReO_3 (rel) are calculated negligible. Therefore, the bonding electrons are rather strongly localized in ReO_3 and that fragment as a whole is a strong and quite hard Lewis acidic site. On the other hand, charge rearrangements are readily induced in CH_3TcO_3 and OsO_4 by lengthening three M−O bonds; these MO_3 fragments are rather polarizable.

Additionally, the dynamic dipole moment, i.e., the displacement derivative of the dipole moment with respect to the M−O bond length, has been calculated. It is a sensitive measure for charge rearrangements in a molecular system and has been widely applied to characterize charge transfer processes in adsorbate/substrate systems, as it can be compared to experimen-

---

(45) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.
(46) Politzer, P. *J. Chem. Phys.* **1987**, *86*, 1072.

tal data on vibrational intensities.[47,48] For all model compounds, the absolute value of the dipole moment increases on M−O bond elongation, an effect that is partly caused by the geometry change. In CH_3TcO_3 and OsO_4, however, the dipole moment increase is more pronounced, indicating an additional contribution due to a charge transfer process between M and O. Following the argument that the induced electron flow along a reaction coordinate becomes more pronounced with increasing softness of the fragments,[30] it is plausible that an attack by a soft Lewis base like an olefin is able to induce the necessary charge rearrangements in the doubly bonded oxo groups of CH_3TcO_3 and OsO_4, but not in the ReO_3 (rel) fragment.

Conclusions

From the present scalar relativistic and nonrelativistic density functional calculations the following key findings on the systems CH_3MO_3 (M = Tc, Re) and their NH_3 adducts can be summarized.

Very good agreement with experiment is obtained on geometrical and vibrational data for CH_3MO_3 (M = Tc, Re) and for their NH_3 base adducts; the Re−C bond is markedly elongated if relativistic effects are not accounted for. A stable base adduct, $E_b = 0.46$ eV, is calculated only for CH_3ReO_3 (rel); shallow minima are found on the energy surface for the other models CH_3ReO_3 (nrel) and CH_3TcO_3 (rel + nrel). According to an analysis of Mulliken populations and of core and valence level shifts, charge transfer from NH_3 occurs preferentially to the Re center is CH_3ReO_3 and to the oxygen atoms in CH_3TcO_3.

From the charge distribution in CH_3MO_3 and in the corresponding NH_3 adducts it can be concluded that Re is the strongest and more reactive Lewis acidic metal center, as it withdraws electronic charge from all its ligands including the electronegative oxygen centers. The hardness, calculated from the HOMO−LUMO splitting and from the M−O displacement derivatives of the charges and of the dipole moment, increases in the order $CH_3TcO_3 < OsO_4 < CH_3ReO_3$. This finding rationalizes the fact that CH_3TcO_3 and OsO_4 react preferentially with softer bases, whereas CH_3ReO_3 prefers to react with hard bases. The experimentally observed reduction of the catalytic activity upon adduct formation between CH_3ReO_3 and a donor base can be explained by the synergistic effect of three factors: the enhanced steric crowding at the metal center and the reduction of both the Lewis acidity strength and the hardness due to charge transfer from the NH_3 fragment.

Viewing together all results of the present investigation there are strong indications that the observed chemoselectivities in olefin oxidation can be explained by reference to the HSAB principle:[27,45] CH_3ReO_3 (rel) exhibits a propensity to react with the harder Lewis base H_2O_2 to the well-known catalytically active mono- and bisperoxo complexes.[40] Instead of oxidizing olefins directly, it even exhibits reactivity with epoxides to react further to glycolate complexes if no H_2O_2 is present.[2,49] From the present findings one expects the same reactivity pattern for other transition metal complexes on the left-hand side of the above mentioned borderline between V/Cr, Mo/Tc, and Re/Os, at least as far as electronegativity χ and hardness η are comparable to the corresponding values for Re. On the other hand, the MO_3 moiety of CH_3TcO_3 and OsO_4 has been calculated to be more polarizable. Hence it is plausible that the preferred reaction partners are soft Lewis bases, e.g., as provided by the π bond of an olefin. The same trend may be anticipated to hold for other transition metals to the right-hand side of the borderline, as well, at least within some limits.

Acknowledgment. We thank K. Albert for her assistance during the preparation of the manuscript. This work has been supported by the Deutsche Forschungsgemeinschaft, by the Bayerische Forschungsverbund Katalyse (FORKAT), and by the Fonds der Chemischen Industrie.

OM9608317

---

(47) Pacchioni, G.; Bagus, P. S.; Nelin, C. J.; Philpott, M. R. *Int. J. Quant. Chem.* **1990**, *38*, 675.

(48) Neyman, K. M.; Rösch, N. *Chem. Phys.* **1993**, *177*, 267.

(49) Zhu, Z.; Al-Ajlouni, A. M.; Espenson, J. H. *Inorg. Chem* **1996**, *35*, 1408.