metric stretches for the NH_2 groups in free thiourea upon complex formation. These bands, which occur at 3097, 3156, 3258, and 3365 cm^{-1} for thiourea, are observed at 3110, 3180, 3260, and 3400 cm^{-1} for the complex, respectively.

Although the parent complex, $AuCl(PEt_3)$, exhibits strong ν(AuCl) bands at 315 and 310 cm^{-1}, no bands are observed in this region, as evident in Figure 2, for the $[Au(tu)(PEt_3)]Cl$ complex. This suggests that the chloride is not coordinated to gold(I) as in the case of $Au(tu)_2Cl$.[39] Most importantly, the medium-intensity infrared band at 268 cm^{-1} for $[Au(tu)(PEt)_3]Cl$ is assigned to ν(AuS), being comparable to that at 284 cm^{-1} for ν(AuS) in the $Au(tu)_2Cl$.[39] Finally, ν(AuP) for $[Au(tu)(PEt_3)]Cl$ is observed at 388 cm^{-1}.

Uncomplexed thiourea has a single, sharp ^1H NMR resonance at δ = 7.18 ppm, which upon complexation shifts downfield to 7.80 ppm. This chemical shift is comparable to that at 7.90 ppm found for the linear S-bonded complex $Ag(tu)_2NO_3$ containing the soft and isoelectronic Ag(I).[38] The NMR data clearly show that the complex $[Au(tu)(PEt_3)]Cl$ does not dissociate in solution to give free thiourea and $AuCl(PEt_3)$ as was believed to occur in chloroform solutions containing the bromide analogue, $Au(tu)(PEt_3)Br$.[13] In addition, these data reveal that the complex remains S-bonded in solution and that the N-bonded isomer does not form.

Conclusions. Of the eight complexes investigated, we have found that the ν(AuP) values in almost all cases fall within 385 ± 5 cm^{-1} and show little sensitivity as a function of the trans ligand and/or charge on the complex. The infrared data do not parallel findings that show ν(AuP) decreases in the order L = Cl > SCN > CN for the trimethylphosphine analogues.[8] These findings are also in further evidence against significant coupling between ν(AuX) or ν(AuL) and ν(AuP).[19,25] In the cases where the ν(AuX) values for $AuX(PEt_3)$ can be compared to those of other complexes of the type $AuX(PR_3)$ and referred to within the text, they agree well with the relative trans influence of ligand Et_3P.[25] In both cases in which the ambidentate ligands SCN^- and $SC(NH_2)_2$ were complexed with $(PEt_3)Au^I$, the soft base, sulfur, selectively bound to the $(PEt_3)Au^I$ moiety as would be expected if the bonding was symbiotic. Finally, assignments for the gold-ligand vibrations in the studied complexes have been made and compared to the relevant literature.

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NMR Relaxation and π Bonding in Group 6 Transition-Metal Hexacarbonyls

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Carbon-13 and oxygen-17 spin-lattice relaxation times were measured for the series $M(CO)_6$, M = Cr, Mo, and W, at two temperatures in the solvent, $CDCl_3$. Values of $T_1(^{13}C)$ at two magnetic field strengths were utilized to calculate reorientational correlation times, τ_c, which, together with $T_1(^{17}O)$, yielded values for the oxygen's quadrupole coupling constant, $\chi(^{17}O)$; results at the two temperatures were in good agreement. The Townes-Dailey theory of QCC's was applied to obtain estimates of the CO's 2π (or π^*) orbital populations, $[2\pi]$, in each of the carbonyls. It was found that the orbital occupancies and, hence, π-bond strengths vary in the order $[2\pi]_{Mo} < [2\pi]_{Cr} \approx [2\pi]_W$. This is the same order observed for the majority of spectroscopic, thermodynamics, and kinetic measures of overall, $\sigma + \pi$, bond energies. Therefore, π-bond variations play an important role in determining the relative M-CO bond stabilities in the group 6 hexacarbonyls.

Introduction

There is now an abundance of evidence that the bonding in transition-metal carbonyl complexes is synergistic in nature, with reinforcement of the otherwise weak σ bond between the CO 5σ and metal d_σ orbitals by metal d_π back-bonding to the CO's 2π framework. Rather surprisingly, though, the relative magnitude of the contributions of the σ and π components to the M-CO bond stability remains poorly understood.[2] This comparative dearth of knowledge is due to the fact that most experimental properties, including the widely used C≡O vibrational force constants[3] and NMR chemical shifts,[4] are affected by variations in both the σ- and π-bond interactions.

Nuclear quadrupole coupling constants (QCC's), defined by $\chi = e^2qQ/h$, are proportional to the electric field gradient (eq) and, thus, directly dependent upon the electronic charge symmetry in the immediate environment of the nucleus.[5] For nuclei involved in multiple bonds, it is generally observed that changes in χ are influenced primarily by variations in π bonding.[5,6]

In recent years, a number of investigators[7,8] have employed NMR spin-lattice relaxation time measurements to estimate oxygen-17 QCC's in a variety of metal carbonyl complexes and have observed that the magnitude of $\chi(^{17}O)$ and, hence, π-bond strengths are markedly dependent upon the metal to which the

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Table I. NMR Relaxation Times and Quadrupole Coupling Constants[a]

complex	T, °C	$T_{1Q}(^{17}O)$,[b] ms	$T_{1A}(^{13}C)$,[c] s	$T_{1B}(^{13}C)$,[d] s	$T_{1CSA}(^{13}C)$,[c] s	$\Delta\sigma$,[e] ppm	τ_c, ps	χ, MHz
$Cr(CO)_6$	21	27.4 (0.6)	16.8 (0.3)	95 (10)	18.5 (0.6)	423	10.1 (0.3)	1.96 (0.04)
	38	31.6 (0.3)	18.8 (0.1)	101 (03)	21.1 (0.2)		8.9 (0.1)	1.94 (0.01) [2.06][f]
$Mo(CO)_6$	21	20.6 (0.1)	15.8 (0.2)	85 (03)	17.7 (0.3)	418	10.8 (0.2)	2.18 (0.02)
	38	24.7 (0.4)	18.2 (0.3)	91 (03)	20.8 (0.5)		9.2 (0.2)	2.16 (0.03) [2.14][g]
$W(CO)_6$	21	24.1 (0.1)	16.5 (0.5)	79 (09)	19.0 (0.9)	395	11.3 (0.5)	1.97 (0.05)
	38	29.3 (0.6)	18.3 (0.2)	79 (07)	21.7 (0.7)		9.9 (0.3)	1.91 (0.04) [2.04][f]

[a] Quantities in parentheses represent one standard deviation. [b] ν_0 = 40.68 MHz (B_0 = 7.05 T). [c] ν_0 = 75.44 MHz (B_0 = 7.05 T). [d] ν_0 = 22.53 MHz (B_0 = 2.11 T). [e] From ref 12. [f] Approximate value. From ref 8b. [g] From ref 8a.

CO is bound, its stereochemical position in the complex, and the type of bonding (e.g. terminal, bridging, or face capping). However, many of the calculated QCC's are approximate and the discussions are generally qualitative in nature; i.e., a smaller value of χ indicates greater d_π–p_π back-bonding.

In order to better assess the capabilities of ^{17}O QCC's to provide quantitative information on π bonding in metal carbonyls, we have undertaken accurate NMR relaxation time measurements of $\chi(^{17}O)$ in the group 6 metal hexacarbonyls, $M(CO)_6$, M = Cr, Mo, and W. The results are used to obtain estimates of the CO 2π orbital populations, which are compared with other spectroscopic, kinetic, and thermodynamic measures of bond strengths in these complexes.

Experimental Section

Relaxation Time Measurements. The compounds were obtained commercially and purified by vacuum sublimation. Samples of each complex were prepared in $CDCl_3$ (c = 0.1–0.2 M) and contained in 10-mm NMR sample tubes. The solutions were degassed by the freeze–pump–thaw technique and sealed under vacuum.

$T_1(^{13}C)$ and $T_1(^{17}O)$ were determined (at natural abundance) on a Varian VXR-300 FT-NMR spectrometer (75.44 MHz for ^{13}C and 40.68 MHz for ^{17}O). To ascertain the reproducibility of calculated coupling constants, all experiments were performed at two temperatures (21 and 38 °C). The standard inversion recovery pulse sequence, $(\pi-\tau-\pi/2-\mathrm{Acq}-t_d)_n$,[9] was used with 10 τ values from 0.1 to 1.5 times the estimated T_1 for each determination; the delay time, t_d, was at least $5T_1$. The number of acquisitions, n, was typically 8 for $T_1(^{13}C)$ and 4096 for $T_1(^{17}O)$. T_1's were calculated, via nonlinear regression, from a fit of the data by a three-parameter magnetization equation.[10] All relaxation times were determined at least three times at each temperature. The results, in Table I, represent the average of the runs.

$T_1(^{13}C)$ was also determined at 22.53 MHz on a JEOL FX-90Q FT-NMR spectrometer. Due to the very long relaxation times, the saturation recovery pulse sequence, $(\pi/2-\tau-\pi/2-\mathrm{Acq})_n$,[9] was used, with n = 16 repetitions. At least two measurements were performed at each temperature.

Calculation of ^{17}O Quadrupole Coupling Constants. The efficiency of spin–lattice relaxation of a quadrupole nucleus is governed by the magnitude of its coupling constant. For the nearly cylindrically symmetric oxygen-17 nuclei ($I = {}^5/_2$) in metal carbonyls, one has for the quadrupolar relaxation rate (T_{1Q}^{-1})[11]

$$T_{1Q}^{-1} = (12\pi^2/125)\chi^2\tau_c \qquad (1)$$

In this equation, χ is the QCC (in Hz) and τ_c is the reorientational correlation time of the C–O vector.

The contribution of chemical shift anisotropy (CSA) to relaxation of the carbonyl's ^{13}C nuclei is dependent upon the same correlation time. Hence, τ_c can be calculated quite accurately from complementary measurements of $T_1(^{13}C)$. Spin rotation (SR) also contributes to relaxation of the carbon-13 nuclei. However, T_{1SR}^{-1} is magnetic field independent whereas $T_{1CSA}^{-1} \propto B_0^2 = aB_0^2$. Therefore, the latter contribution may be isolated by measurements at two values of B_0 via the relation $T_1^{-1}(^{13}C) = T_{1SR}^{-1} + aB_0^2$. T_{1CSA} is related to the rotational correlation time by[11]

$$T_{1CSA}^{-1} = (2/15)\gamma^2 B_0^2(\Delta\sigma)^2\tau_c \qquad (2)$$

γ is the ^{13}C magnetogyric ratio and $\Delta\sigma$ is the chemical shift anisotropy ($\Delta\sigma = \sigma_\parallel - \sigma_\perp$). Using measured relaxation times and reported values for $\Delta\sigma$,[12] we have determined τ_c for the three complexes at both temperatures studied. These correlation times, together with $T_{1Q}(^{17}O)$ were then employed in eq 1 to calculate QCC's in the group 6 hexacarbonyls.

Results and Discussion

Quadrupole Coupling Constants. Displayed in the last column of Table I are the calculated quadrupole coupling constants in the group 6 hexacarbonyls. The standard deviations in χ (in parentheses) are derived from errors in the individual relaxation times. Results at the two temperatures are almost identical in the Cr and Mo complexes. There is greater deviation in $W(CO)_6$ due to larger error in $T_{1B}(^{13}C)$. However, the two values agree to within their standard deviations.

Also shown (in square brackets) in Table I are QCC's reported earlier by Brownlee et al.[8a,b,13] Their value for $\chi(^{17}O)$ in $Mo(CO)_6$,[8a] derived from combined ^{17}O and ^{13}C T_1 measurements (in $CDCl_3$ at 40 °C), is in excellent agreement with ours. On the other hand, their QCC's for the Cr and W complexes[8b] were derived from $T_1(^{17}O)$ alone by using correlation times extrapolated from $Mo(CO)_6$ via the Debye–Stokes equation.[14] Thus, it is not surprising that these approximate results for $\chi(^{17}O)$ deviate substantially from the exact values obtained in the present investigation and underestimate the total variation in χ within the series by a factor of 2.

Estimation of CO 2π-Orbital Populations from $\chi(^{17}O)$. Earlier investigators have interpreted $\chi(^{17}O)$ in metal carbonyls qualitatively, noting that a smaller QCC reflects greater d_π–p_π back-bonding. However, it is possible to apply the classic Townes–Dailey[15] (T–D) formalism to derive semiquantitative estimates for $[2\pi]$ (or $[\pi^*]$), the occupancy of the carbonyl's antibonding π molecular orbital.

For a second-row monocoordinated triply bonded nucleus (e.g. ^{14}N in C≡N or ^{17}O in C≡O) with sp type σ-bonding/lone-pair hybrid orbitals directed along the z axis, application of the T–D approximations yields the following expression for the QCC:[5,6]

$$\chi = (p_\sigma^\circ - p_\pi/2)\chi_0 \qquad (3)$$

χ_0 represents the coupling constant of a single electron in a p orbital (20.9 MHz[16] for ^{17}O). $p_\sigma^\circ = p_\sigma(1-\alpha^2) + 2\alpha^2$, where α^2 and p_σ are the fractional s character and the p_z orbital population in the σ-bonding orbital. p_π represents the sum of the π-bonding p-orbital populations ($p_\pi = p_x + p_y$) on the oxygen nucleus; we note that p_π is less than the total occupancy, $[2\pi]$, of the antibonding MO (vide infra). From this equation, one sees that, in principle, variations in either the σ- or π-bondig p-orbital populations will effect changes in χ. However, Cheng and Brown,[6a] using nuclear quadrupole double resonance spectroscopy, have

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Table II. Comparative Measures of M–CO Bond Strengths in Group 6 Metal Hexacarbonyls

complex	$[2\pi]_\chi$[a]	F_{MC}[b]	F_{CO}[b]	$\Delta H^*[A]$[c,f]	$\Delta H[B]$[c,i]	$\Delta H^*[C]$[c,j]	$\Delta H°[D]$[c,m]	$\Delta H^*[E]$[c,n]
$Cr(CO)_6$	0.380 (0.006)	2.10[d]	17.04[d]	168[g]	155	197[k]	108	362
			16.95[e]	162[h]		154[l]		
$Mo(CO)_6$	0.346 (0.005)	2.00[d]	17.15[d]	133[g]	142	169[k]	152	324
			16.96[e]	126[h]				
$W(CO)_6$	0.382 (0.008)	2.32[d]	17.02[d]	167[g]	159	192[k]	178	360
			16.84[e]	167[h]				

[a] Derived from average χ (Table I). Quantities in parentheses represent one standard deviation. [b] In units of mdyn/Å. [c] In units of kJ/mol. [d] GQVFF force constants. Reference 20. [e] Force constants from energy-factored force field. Reference 20. [f] Activation enthalpy for bond dissociation from thermal kinetics. [g] From dissociative substitution by PBu^n_3. Reference 21. [h] From dissociative ^{14}C exchange. Reference 22. [i] Bond dissociation enthalpy from laser photoacoustic calorimetry. Reference 24. [j] Activation enthalpy from laser pyrolysis. Reference 23. [k] Observed value. [l] Value recalculated by assuming a two-step mechanism and a transferred value for the preexponential factor, *A*. [m] Mean thermochemical bond enthalpy. Reference 25. [n] Mean "intrinsic" bond enthalpy. See text.

investigated a series of 23 organic carbonyl compounds. Through measurement of both χ and η (the field gradient asymmetry factor) and use of expressions analogous to eq 3 above, they observed that, whereas p_π was found to vary widely, $p_\sigma°$ remained virtually constant through the series. The same invariance of $p_\sigma°$ was observed in similar studies of $\chi(^{17}O)$ in substituted nitrobenzenes[6b] and in carboxylic acids.[6c] Thus, there is ample experimental evidence that changes in ^{17}O-coupling constants in multiply bonded organic compounds are influenced predominantly by variations in the π-electron distribution. In the following analysis, we shall assume that variations in the ^{17}O QCC's of transition carbonyls, too, are predominated by variations in M–CO π bonding. This assumption is supported by the theoretical calculations of Caulton and Fenske[17] on the series $Mn(CO)_6^+$, $Cr(CO)_6$, and $V(CO)_6^-$.

One expects changes in the total 2π-antibonding molecular orbital population to be proportional to variations in p_π; i.e., $\Delta[2\pi] = \xi(\Delta p_\pi)$. When it is recognized that $\chi_{CO} = 4.43$ MHz[18] corresponds to $[2\pi]_{CO} = 0$, eq 3 may be applied directly to obtain the following simple expression relating a carbonyl's 2π occupancy to χ:

$$[2\pi]_\chi = 2\xi\frac{\chi_{CO} - \chi}{\chi_O} \qquad (4)$$

The subscript on the left-hand side of the equation has been added to indicate that $[2\pi]$ has been calculated from the ^{17}O QCC. The value for the proportionality constant, ξ, may be calculated from the measured QCC in $Cr(CO)_6$, together with the quasi-experimental 2π population in this complex, $[2\pi]_{Cr(CO)_6} = 0.38$ electron, obtained from X-ray and neutron diffraction.[19] With our average QCC, $\chi = 1.95$ MHz, for chromium hexacarbonyl (Table I), one finds that $\xi = 1.60$. Calculated orbital occupancies, $[2\pi]_\chi$, for $Mo(CO)_6$ and $W(CO)_6$ are presented in Table II. We note that since the 2π-antibonding MO contains a greater electron density on the carbon than on the oxygen atom, one expects that the proportionality factor relating changes in $[2\pi]$ to variations in p_π should be greater than 2; i.e., $\Delta[2\pi] = \xi(\Delta p_\pi) > 2(\Delta p_\pi)$. That $\xi < 2$ probably results from errors in the experimental value of $[2\pi]$[19] and/or simplifications in the Townes–Dailey approach.

It is seen that 2π populations and, hence, π-bond strengths in the chromium and tungsten hexacarbonyls are virtually equal to each other and greater than $[2\pi]_\chi$ in $Mo(CO)_6$ by approximately 10%, which is well outside the range of experimental error (as indicated by the standard deviations).

Comparison with Other Results. It is informative to compare the π-bond strengths determined from $\chi(^{17}O)$ with the results from spectroscopic,[20] kinetic,[21-23] and thermodynamic[24,25] investigations of the group 6 hexacarbonyls. The quantities derived from these latter experiments, which are considered to be dependent upon the total ($\sigma + \pi$) strength of the M–CO bond, are presented in Table II.

One observes that the MC and CO GQVFF vibrational force constants[20] (F_{MC} and F_{CO}) both indicate that *net* bonding is weakest in the Mo complex, consistent with π-bond strengths obtained here; EFFF CO force constants[20] show a somewhat different trend. First, ligand dissociation enthalpies determined from standard substitution[21] and exchange[22] kinetics ($\Delta H^*[A]$) display a minimum for molybdenum hexacarbonyl. Dissociation enthalpies ($\Delta H[B]$) obtained from laser photoacoustic calorimetry experiments[23] exhibit the same trend. On the other hand, a recent laser pyrolysis study[24] yields results ($\Delta H^*[C]$) that may be contrary to earlier kinetic data.[21,22] The observed activation energies (and enthalpies) vary in the same order as those of other kinetics experiments (Mo < Cr ≈ W). However, because of an unusually large preexponential factor for the decomposition of $Cr(CO)_6$, the authors reinterpreted their results on this complex on the basis of a proposed two-step mechanism and concluded that activation enthalpies vary in the order Cr < Mo < W.

The uniform rise in the mean thermochemical bond enthalpies[25] ($\Delta H°[D]$) is often cited as evidence that the net bond strengths increase monotonically in the group 6 hexacarbonyls. However, it has been pointed out by various investigators[2,25,26] that one should actually consider trends in the "intrinsic" bond enthalpy, ΔH^*(M–CO). This quantity represents one-sixth of the enthalpy change for the hypothetical process $M(CO)_6(g) \rightarrow M^*(g) + 6CO^*(g)$, where M^* represents the metal in the $t_{2g}{}^6$ configuration and CO^* is carbon monoxide in its bonded valence state. It is related to the measured bond enthalpy by $\Delta H^*(M{-}CO) = \Delta H°(M{-}CO) + \Delta H_{CO^*}{}^M + \Delta H_{M^*}$. The CO valence reorganization enthalpy, $\Delta H_{CO^*}{}^M$, has been estimated for all three complexes and is approximately constant.[25b,27] Connor and coworkers[25b] have also calculated an approximate value (160 kJ/mol) for the metal's valence promotion enthalpy, ΔH_{M^*}, for $Cr(CO)_6$ from spectroscopic state energies and calculated metal charges: currently, there are insufficient data to apply this technique to the 4d or 5d metals.[25b,28] Recently, however, Ziegler et al.[2] have calculated theoretical promotion enthalpies for all three metals and found that $\Delta H_{M^*}(Mo) \approx \Delta H_{M^*}(W) \approx {}^1/_2\Delta H_{M^*}(Cr)$. They attributed the substantially greater value for Cr to the stronger interelectronic repulsions resulting from the significantly lower spatial extension of this metal's 3d orbitals relative to the 4d and 5d orbitals in Mo and W. Their conclusion is supported by trends in the Racah parameter ($B_{Cr} \gg B_{Mo} \approx B_W$)[29] in both the free ions and the hexacarbonyls.

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It is possible to estimate ΔH^*(M–CO) from the measured bond enthalpies, ΔH°,[25] estimated valence reorganization enthalpies, $\Delta H_{\mathrm{CO}\bullet}{}^{\mathrm{M}}$,[27] and the approximation $\Delta H_{\mathrm{M}\bullet}(\mathrm{Mo}) \approx \Delta h_{\mathrm{M}\bullet}(\mathrm{W}) \approx 80$ jK/mol (i.e. $^1/_2\Delta H_{\mathrm{M}\bullet}(\mathrm{Cr})$). These values for the "intrinsic" bond enthalpies (ΔH^*[E] in Table II) exhibit the order Mo < Cr ≈ W. Thus, the thermochemical bond enthalpy data are consistent with trends in bond enthalpies from spectroscopic and kinetic measurements *if*, as calculated by Ziegler et al.,[2] the valence promotion energy for Cr is substantially greater than for the 4d and 5d metals.

Conclusions

It has been suggested, on the basis of experimental IP's and charge-transfer spectra, that the π bond order increases monotonically within the group 6 metal hexacarbonyls.[29] However, we have observed here that the CO 2π-orbital populations calculated from $\chi(^{17}\mathrm{O})$ vary in the order $\mathrm{Mo(CO)_6} < \mathrm{Cr(CO)_6} \approx \mathrm{W(CO)_6}$. This is the same order found for the majority (although not totality) of experimental quantities dependent upon the net, $\sigma + \pi$, M–CO bond strengths. From this comparison, one may conclude that variations in π bonding play an important role in determining relative bond strengths in group 6 hexacarbonyls. We note that this lends a degree of support for the results of recent theoretical investigations[2] which suggest that the total stability of the M–CO bond in transition-metal complexes is dominated by the π component.

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Molecular Orbital Investigation of Ruthenium–Oxo-Catalyzed Epoxidations

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INDO/1 calculations were carried out with the aim of studying the various intermediates and pathways proposed for epoxidations involving high-valent, metal–oxo catalysts: *N*-oxo, oxometallacycle, open, bound epoxide, and caged radical intermediates. The model complex chosen was a six-coordinate Ru(IV)–oxo complex. The conversion of the Ru–oxo complex to a five-coordinate *N*-oxo intermediate was discounted due to the large energy barrier to migration of O to the nitrogen atom of a ligand. The formation of the oxometallacycle by a either a concerted or nonconcerted pseudo-[2 + 2] cycloaddition of C═C to Ru—O was found to be unfavorable. A concerted [1 + 2] addition was also found to be unfavorable. The calculations show that the unfavorable nature of these pathways is similar in origin to that of their better known organic analogues. The preferred pathway is a nonconcerted [1 + 2] cycloaddition to yield a bound epoxide. The reaction amounts to nucleophilic attack on the oxo oxygen. Since one C–O bond is formed first, and then the second, there is a buildup of radical cation behavior on the carbon that is not bound. Simple electrostatic considerations lead one to predict, and INDO/1 calculations agree, that attack of the unbound carbon on the electron-rich oxo (to yield bound epoxide by a nonconcerted [1 + 2] pathway) in preference to the high-valent Ru atom (to yield oxometallacycle by a nonconcerted [2 + 2] pathway). The results of the theoretical analysis are combined with experimental data in an attempt to clarify the important interactions that characterize this important reaction.

Introduction

Epoxidation is a commercially important process. In the year 1987, 5.62 billion pounds of ethylene oxide and 2.61 billion pounds of propylene oxide were produced in the United States.[1] The mechanisms by which the enzyme cytochrome P-450 and its inorganic porphyrin analogues oxidize various organic species has been an area of much focus.[2] Epoxidation of olefins, in particular, has gathered much attention.[3] The discovery by Groves and co-workers that $\mathrm{Fe^{III}(TPP)Cl/PhIO}$ (TPP = tetraphenylporphyrin) can perform chemistry similar to that of the cytochrome P-450/molecular oxygen system has fostered much research into the proposed Fe–oxo reactive intermediate.[4] Other workers have concentrated on different metals[5] and different oxygen atom transfer reagents.[6]

For epoxidations involving these metal–oxo complexes, many pathways and intermediates arising from the oxygen atom transfer step have been discussed. The [2 + 2] cycloaddition of the olefins to the metal–oxo bond to yield a four-membered ring structure, referred to alternatively as an oxometallacycle or metallaoxetane,[7] has been proposed. The work of Bruice[8] with *N*-oxo transfer reagents has led to the consideration of a process where a precursor with increased N (from a ligand)–O bonding is the active species. Direct oxygen atom transfer has been advanced to explain the stereospecificity of some systems,[9] while open intermediates have been invoked to explain stereochemical inversion in others.[10] Outer-sphere electron transfer,[11] to form a caged radical cation species, and a suicide complex[12] —a cyclic, five-membered, M-O-C-C-N intermediate—have also been forwarded.

Ruthenium-oxo catalysts have recently been reported that utilize molecular oxygen to epoxidize norbornadiene and styrene.[13,14] We have carried out semiempirical molecular orbital calculations on a Ru(IV)–oxo complex with the intent of studying the various pathways and intermediates that have been postu-

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