Oxygen transfer in electrophilic epoxidation probed by $^{17}$O NMR: differentiating between oxidants and role of spectator metal oxo†

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Peroxide compounds are used both in laboratory and industrial processes for the electrophilic epoxidation of olefins. Using NMR-spectroscopy, we investigate why certain peroxides engage in this type of reaction while others require activation by metal catalysts, e.g. methyltrioxorhenium (MTO). More precisely, an analysis of $^{17}$O NMR chemical shift and quadrupolar coupling parameters provides insights into the relative energy of specific frontier molecular orbitals relevant for reactivity. For organic peroxides or H$_2$O$_2$ a large deshielding is indicative of an energetically high-lying lone-pair on oxygen in combination with a low-lying O–O bond. This feature is particularly pronounced in species that engage in electrophilic epoxidation, such as peracids or dimethyldioxirane (DMDO), and much less pronounced in unreactive peroxides such as H$_2$O$_2$ and ROOH, which can however be activated by transition-metal catalysts. In fact, for the proposed active peroxo species in MTO-catalyzed electrophilic epoxidation with H$_2$O$_2$ an analysis of the $^{17}$O NMR chemical shift highlights specific O–O and O–H type orbital interactions between the so-called metal spectator oxo and the peroxy moieties that raise the energy of the high-lying lone-pair on oxygen, thus increasing the reactivity of the peroxy species.

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Recent work has shown that analysis of the $^{13}$C NMR chemical shift tensor (CST) of metal alkyl compounds can give valuable insights into the electronic structure and the reactivity of ubiquitous reaction intermediates in organometallic chemistry and homogeneous catalysis. Considering the large chemical shift window of $^{17}$O nuclei (around 1200 ppm), we reasoned that analysis of the $^{17}$O NMR chemical shift tensor of oxidants would allow for a detailed understanding of the electronic structure and associated reactivity of these molecules. In addition, the quadrupolar coupling constant of $^{17}$O (nuclear spin $I = 5/2$) can provide valuable information on the charge distribution around the nucleus.

Fig. 1 (a) Representative primary peroxide oxidants used for electrophilic epoxidation, (b) MTO-catalyzed olefin epoxidation involving bisperoxo- or monoperoxo-species (L = pyridine or water).

Introduction

Electrophilic epoxidations are at the core of numerous processes, ranging from the industrial synthesis of propylene oxide to enzymatic oxygenase reactions. In organic synthesis, this ubiquitous transformation is commonly achieved by using stoichiometric epoxidation agents such as meta-chloroperbenzoic acid (mCPBA), dimethyldioxirane (DMDO), or azoxiridines. H$_2$O$_2$ and ROOH can also be used for epoxidation but they require a catalyst. The most commonly used catalysts are (i) organorhenium trioxides (especially methyltrioxorhenium, MTO) and group 6 metal dioxo compounds (Fig. 1) or (ii) early transition-metal alkoxides (e.g. Ti and V) that involve peroxy-species as key reaction intermediates.

While the reactivity of oxidizing agents such as mCPBA or DMDO towards olefins is well established and exploited synthetically, the origin of their reactivity towards C–C double bonds has not been studied in detail. This question is particularly apparent when considering that other peroxides, such as H$_2$O$_2$ or tBuOOH, are usually not reactive towards olefins, unless combined with metal catalysts.

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spectroscopy has been used to identify and study peroxy species as well as related compounds containing O–N bonds.\textsuperscript{41–46}

The isotropic chemical shift $\delta_{\text{iso}}$ (eqn (1)) and the three principal components ($\delta_{11} \geq \delta_{22} \geq \delta_{33}$) of the CST contain a considerable amount of information on the electronic structure of NMR active nuclei. The corresponding shielding values ($\sigma$, eqn (2)), can be decomposed computationally into diamagnetic ($\sigma_{\text{dia}}$) and paramagnetic contributions, which also include contributions from spin–orbit coupling ($\sigma_{\text{para}+\text{SO}}$, eqn (3)). While the diamagnetic contributions, which arise from a molecule’s electronic ground state, lead to shielding and are usually similar for all nuclei of a given kind independent of their chemical environment, the paramagnetic contributions, which give mostly rise to deshielding, originate from magnetically induced coupling of excited states to the ground state, by action of the angular momentum operator $L_i$ as described in a 2nd order perturbation approach in eqn (4).\textsuperscript{37}

\[
\begin{align*}
\delta_{\text{iso}} &= \frac{1}{3} (\delta_{11} + \delta_{22} + \delta_{33}) \\
\delta_i &= \sigma_{\text{dia}} - \sigma_i \quad (i = 1, 2, 3) \\
\sigma &= \sigma_{\text{dia}} + \sigma_{\text{para}+\text{SO}} \\
\sigma_{\text{para}} &= \frac{\langle \psi_{\text{oct}} | L_i | \psi_{\text{oct}} \rangle \langle \psi_{\text{oct}} | \hat{L}_i | \psi_{\text{oct}} \rangle}{\Delta E_{\text{oct-oct}}} = \frac{eQ}{\Delta E_{\text{oct-oct}}} 
\end{align*}
\]  

According to eqn (4), deshielding of a nucleus is expected along the direction $i$, if an occupied orbital on this nucleus can be “superimposed” onto a vacant orbital on the same nucleus rotated by $90^\circ$ along the axis $i$ (Fig. 2). Since the extent of deshielding increases with a decreasing energy gap between the two orbitals, the paramagnetic contribution to shielding is most strongly affected by frontier molecular orbitals (FMOs) – energetically high-lying occupied and low-lying vacant orbitals.

In this work, we make use of chemical shift to evidence specific high-lying occupied and low-lying vacant orbitals in the aforementioned oxidizing agents, thereby probing their electronic structure and connection to the observed reactivities.

As $^{17}$O is a quadrupolar nucleus ($I = 5/2$), the quadrupolar coupling, which typically complicates the interpretation of spectra by line broadening, holds information about the distribution of charges around the nucleus. The quadrupolar interaction is proportional to the electric field gradient (EFG) tensor $V$ (eqn (5)), where $e$ is the electron charge, $Q$ is the quadrupolar moment of $^{17}$O, $h$ is the reduced Planck constant ($h = \hbar/2\pi$), $I$ is the nuclear spin operator and $I$ the nuclear spin quantum number.

\[
\hat{H}_0 = \frac{eQ}{2I(2I-1)\hbar} IVI \tag{5}
\]

$V$ is a traceless second rank tensor ($V_{11} + V_{22} + V_{33} = 0$) where we follow the notation $|V_{33}| \geq |V_{22}| \geq |V_{11}|$ for the three principal components. The EFG tensor can be described by two independent variables – usually the largest principal component ($V_{33}$) and the asymmetry parameter $\eta$ (eqn (6)).

\[
\eta = (V_{11} - V_{22})/V_{33} \tag{6}
\]

The quadrupolar coupling constant $C_Q$ arises from the interaction of the quadrupole moment of $^{17}$O ($I = 5/2$) with the EFG and is proportional to $V_{33}$ (eqn (7)). Since the electric quadrupole moment $Q$ of the $^{17}$O nucleus is negative, $V_{33}$ and $C_Q$ have opposing signs.

\[
C_Q = (eQV_{33}/h) \tag{7}
\]

$V_{33}$ and hence $C_Q$ are indicative of how symmetric the EFG and thus the charge distribution around the nucleus is. This has been a valuable tool to assess local symmetry around quadrupolar nuclei (e.g. $^{17}$O, $^{27}$Al, $^{45}$Sc).\textsuperscript{38,41,42,46–51}

### Results & Discussion

#### CSTs of non-metal-based peroxides

We calculated the chemical shift tensors (CSTs) of selected peroxides relevant to epoxidation reactions, as well as associated reduced compounds. We chose to investigate DMDO and mCPBA, two compounds showing activity towards electrophilic epoxidation, as well as $\text{H}_2\text{O}_3$ and $\text{tBuOOH}$ that do not participate in this transformation, unless activated by metal catalysts. In order to benchmark our calculations, we also experimentally determined the $^{17}$O NMR chemical shift tensors of $\text{H}_2\text{O}_3$\textsuperscript{52} and acetone by solid-state $^{17}$O NMR spectroscopy\textsuperscript{53–55} (see ESI† for experimental details).

The measured and calculated chemical shifts are given in Table 1. Generally, a good agreement between calculated and experimental data (when available) is obtained. The oxygen atoms of the unsymmetric peroxides ($\text{tBuOOH}$ and $m\text{CPBA}$) are labelled (O), for the oxygen bound to a carbon atom and (OH) for the oxygen connected to the hydrogen.

A comparison of the isotropic chemical shifts given in Table 1 reveals that all peroxy species ($\text{H}_2\text{O}_3$, $\text{tBuOOH}$, $m\text{CPBA}$, and DMDO) show significantly more deshielded $\delta_{\text{iso}}$ values in comparison with $\text{H}_2\text{O}_3$, $\text{tBuOH}$ and $m\text{CBA}$, albeit less deshielded than carbonyl oxygens (e.g. mCBA (C=O) and acetone). While the differences among the various peroxides are less pronounced, the chemical shift ($\delta_{\text{iso}}$) of the oxygen atom which is transferred during epoxidation reactions is more deshielded for DMDO and $m\text{CPBA}$ (OH) as compared to $\text{H}_2\text{O}_3$ and $\text{tBuOOH}$ (OH). A closer inspection of the principal components of the chemical shift tensor reveals that this is mostly due to the $\delta_{11}$
component of the CST which is significantly more deshielded in DMDO and the OH–oxygen of mCPBA (636 and 540 ppm) than in H2O2 and tBuOOH (364 and 386 ppm). This highly deshielded component is accompanied by a significantly larger span of the CST in the former compounds.

**Orientation of the CSTs**

In order to further understand these observed trends, we investigated the orientation of the 17O NMR chemical shielding tensors (CSTs) as obtained by DFT calculations. The calculated CSTs are shown in Fig. 3. Notably, the 17O CST is similarly oriented in all the aforementioned peroxides, with the most deshielded δ11 component being oriented perpendicular to the O–O axis and lying in the O–O–H/R plane. The δ33 component points along the O–O axis, while δ22 is perpendicular to both, δ11 and δ33. Minor deviations to this pattern are found for mCPBA (O) and DMDO, where the orientation of the δ11 and δ33 components is slightly tilted, by comparison with the other compounds (vide infra).

**Orbital analysis of the CSTs**

We decided to further elucidate the origin of deshielding in the individual components of the CST in a Natural Chemical Shielding (NCS) analysis.47,48,60–65 This analysis allows for a decomposition of the σδδ component into diamagnetic (σdia) and paramagnetic/spin–orbit (σpara+SO) contributions (eqn (3)). The paramagnetic term can then be further decomposed into contributions of the various NLMOs (bonds and lone pairs) surrounding the nucleus of interest. Due to the orbital energy difference in the denominator of eqn (4), the orbitals contributing most strongly to σpara+SO are the frontier molecular orbitals (FMOs) of the molecule with a non-vanishing coefficient on the investigated nucleus.

Since the largest differences in the CST of the investigated peroxides originate from the σ11/δ11 component of the CST, its orbital analysis will be further discussed (see Fig. S3 and S4† for other components).

The NCS analysis of the σ11 component of the various compounds (Fig. 4b) reveals, that the diamagnetic contributions to this component are essentially invariant throughout the whole series of compounds. The differences in δ11 result from the paramagnetic contributions, which are mainly affected by four different Natural Localized Molecular Orbitals (NLMOs). These correspond to two lone-pairs on oxygen (denoted as LP ‘p’ and LP ‘s’), as well as the two σ-bonding orbitals (denoted as σ(O–R) and σ(O–O)). These four NLMOs are visualized for the case of hydrogen peroxide in Fig. 4a; for the other compounds they are shown in Fig. S11–S13†.

Notably, the dominant contribution to the deshielding of σ11/δ11 originates from the LP ‘p’ on oxygen in all cases given in Fig. 4, with the exception of mCPBA (O) (vide infra). The observation of the large deshielding perpendicular to the O–O axis originating from this lone pair indicates the presence of a low-lying vacant orbital, oriented perpendicular to both the lone-pair and the direction of σ11/δ11; i.e. oriented along the O–O bond (eqn (4)). This vacant orbital corresponds to σ* (O–O), the lowest unoccupied molecular orbital with contribution of oxygen in all of the investigated peroxides. As the extent of
The LP indicates a deviation of the localized orbital from the internuclear (NHO) Directionality and Bond Bending Analysis which the CST component signifies the deviation of the orbital from the internuclear axis by 16.8°, as opposed to 2.5° in the case of H₂O₂ (the values for other investigated compounds are given in Table S6†).

### Energetic considerations in oxygen-transfer reactions

The strong deshielding of the δ₁₁ component in the case of DMDO and mCPBA evidences a particularly low-lying σ*(O–O) orbital in combination with a high-lying lone pair LP ‘p’ in these compounds. In order to further understand the impact of this orbital situation on reactivity we investigated the corresponding transition states for the epoxidation of ethylene with DMDO and mCPBA. In both transition states, the olefin is oriented perpendicularly to the plane consisting of the peroxo moiety and the respective substituents (Fig. 5). The free energies of activation for DMDO and mCPBA are found at 25.6 and 25.7 kcal mol⁻¹, respectively.

The geometry of these transition states can be rationalized by the orbital situation derived from the CST analysis: while a low-lying σ*(O–O) orbital of the peroxide allows for a good interaction with the π(C=O) bond of the olefin, the oxygen lone pair LP ‘p’ involved in the filled π*(O–O) orbital can interact with the empty π*(C=O) orbital (Fig. 6). Both of these interactions are energetically favorable and are expected to lower the transition state energy for olefin epoxidation. The deshielded δ₁₁ component of the CST is thus indicative of the epoxidation propensity of DMDO and mCPBA.

The 17O NMR chemical shift of the investigated peroxides shows that DMDO and mCPBA, the two molecules engaging in electrophilic epoxidation, feature a high-lying lone pair LP ‘p’ and a low-lying σ*(O–O) orbital. This observation can be understood based on the geometry of these compounds: In DMDO and mCPBA the lone pairs LP ‘p’ of the peroxo oxygens are co-planar, resulting in a maximized filled–filled interaction (π-effect), and thus a high-lying filled antibonding π*(O–O) orbital. Hence, in the epoxidation process, the backdonation of the lone pair of the attacked oxygen into the π*(C=O) of the olefin is more efficient for these reagents.

The importance of this “backdonation” was further explored by investigating transition state geometries where the olefin is perpendicular to the oxygen lone pair and hence co-planar with the dioxirane moiety in DMDO or the carbonyl group in mCPBA. The corresponding transition state (2nd order saddle point) energies for the epoxidation where the rotation around the reaction coordinate was restricted were found at 32.7 and 29.0 kcal mol⁻¹ for DMDO and mCPBA, respectively. The

![Fig. 4](image-url) (a) Relevant NLMOs contributing to the paramagnetic shielding of the investigated peroxides. (b) Results of the NCS analysis of the most deshielded component of the shielding tensor, σ₁₁, represented in a bar diagram.

![Fig. 5](image-url) Transition state geometries for the electrophilic epoxidation with (a) DMDO and (b) mCPBA.

![Fig. 6](image-url) Relevant orbital interactions in epoxidation, shown for the case of DMDO. Electron-donating and -accepting orbitals are colored in red and blue, respectively.
backdonation of the LP ‘p’ into the π*(C–C) of the olefin hence gives rise to a significant stabilization of the transition state energy in both cases (7.1 kcal mol⁻¹ for DMDO and 3.3 kcal mol⁻¹ for mCPBA).

### Quadrupolar coupling parameters

To complement the analysis of the $^{17}$O NMR parameters we calculated the quadrupolar coupling parameters of the aforementioned peroxides. The respective $^{17}$O $C_Q$ and $\eta_Q$ values are reported in Table 2.

For all investigated peroxide oxygens, the absolute magnitude of the quadrupolar coupling constant $C_Q$ (and $V_{33}$ accordingly) is significantly larger than for water. The orientation of the EFG tensor is similar in all of these peroxides, with the most positive component oriented along the O–O bond, and the most negative component oriented in the direction of LP ‘p’ (selected examples in Fig. 7a–c, see Fig. S14† for other compounds). This orientation is hence indicative of a region of high electron density in the direction of LP ‘p’, and a region of depleted electron density in the direction of the O–O bond. The reversed sign of $C_Q$ observed for DMDO in contrast to other peroxides is due to the definition of $V_{33}$, which always corresponds to the EFG tensor component with the largest absolute value (indicated by a red arrow in Fig. 7). While the EFG tensor is similar in all peroxides, the negative EFG tensor component perpendicular to the O–O bond is slightly larger for DMDO by absolute value as compared to the positive EFG tensor component along the O–O bond. For the other investigated peroxides, the situation is reversed, leading to a change in sign of $V_{33}$ and hence of $C_Q$. The large $C_Q$ value for peroxides in combination with the specific orientation of the EFG tensor is consistent with the presence of a high-lying occupied orbital (LP ‘p’) oriented perpendicular to a low-lying vacant $\sigma^*(O–O)$ orbital in these species. This observation parallels what is seen from the NCS analysis of the $\delta_{11}$ component of the CST.

### MTO-catalyzed epoxidation

As both H$_2$O$_2$ and tBuOOH are inactive in electrophilic epoxidation but are rendered active in the presence of transition-metal catalysts, we investigated the process of activation and the properties of the proposed active species. We chose methyltriioxorhenium (MTO) as a prototypical catalyst because of its high efficiency in olefin epoxidation with H$_2$O$_2$ (Fig. 1b), and the existence of detailed mechanistic studies (isolation of reaction intermediates, measurements of $^{17}$O NMR parameters and computational studies).$^{15,68–71}$ We hence calculated the chemical shift tensors of MTO (Table 3 and Fig. 8e) and of the water and pyridine adducts of the corresponding mono- and bisperoxides (Table 3). The bisperoxo pyridine adduct will be discussed in more detail; the tensors are shown in Fig. 8a and b.$^{17,39,72}$ The CSTs and NCS analyses for other intermediates are provided in the ESIF (Table S1, Fig. S1 and Tables S2–S4, Fig. S8–S10,† respectively) and further commented below for comparison.

### CST of peroxo intermediates

The measured and calculated chemical shifts of bis- and monoperoxo intermediates of the MTO-catalyzed olefin epoxidation are given in Table 3. Both the isotropic chemical shift ($\delta_{iso}$) and the three principal components of the CST are significantly more deshielded in the metal-peroxide compound by comparison with H$_2$O$_2$ (Table 3, where cis/trans denotes the peroxo oxygen pseudo-cis/trans with respect to the methyl substituent). This observation suggests a change in the electronic structure of the peroxide oxygen atoms, which is likely connected to their increased reactivity towards olefins. Note the significantly larger deshielding found for the oxo-ligands as typically observed for metal-oxo compounds.$^{73,74}$ The CSTs of the peroxo oxygen atoms have similar orientations as shown in Fig. 8 (and Fig. S1 for the water adducts and the monoperoxo species). For both peroxo oxygens, $\sigma_{11}/\delta_{11}$ and $\sigma_{33}/\delta_{33}$ are in the O–Re–O plane (defined by Re and the two peroxo O-atoms) whereas $\sigma_{22}/\delta_{22}$ is perpendicular to it. In contrast to H$_2$O$_2$, the most deshielded component of the metal peroxo species, $\delta_{11}$, is no longer oriented perpendicularly to the O–O axis but is significantly tilted, while remaining in the peroxo O–Re–O plane. One can also note differences of chemical shifts observed for the cis and trans peroxo oxygens in the bisperoxo compounds, the former being slightly more deshielded than the latter for both $\delta_{iso}$ and $\delta_{11}$. These values are not strongly affected by the apical ligand (pyridine vs. water), suggesting a similar electronic structure in all bisperoxo intermediates. For the monoperoxo species, the $\delta_{iso}$ of both peroxo oxygens are more similar, albeit slightly more deshielded than in the bisperoxo intermediates.

### Orbital analysis of the CSTs

An orbital analysis reveals that the largest contribution to the paramagnetic deshielding of the $\sigma_{11}/\delta_{11}$ component arises from
As observed for non-metal-based peroxides, the MTO-derived bisperoxide shows rather large $C_Q$ values (−15.0 MHz and −15.2 MHz for the cis- and trans-oxygen, respectively, see Table S5 and Fig. S15†) by comparison with MTO (−4.6 MHz). This again indicates a large electric field gradient around the peroxide O-atoms, consistent with a high-lying lone pair oriented

While the contributions of the LP ‘p’ is again indicative of a low-lying $\sigma^*(O-O)$ orbital in combination with high-lying lone-pairs LP ‘p’ on oxygen, the significant contribution of the $\sigma(O-Re)$ bond to $\sigma_{11}$ evidences the presence of a low-lying vacant orbital perpendicular to the O-Re-O plane with oxygen-contribution. A closer inspection reveals that the bonding combination of the oxygen lone pairs LP ‘p’ perpendicular to the O-Re-O plane – $\pi$(O-O) – can interact with an empty metal d-orbital (i.e. $d_{yz}$) forming a $\pi$-bond while the anti-bonding combination of the LP ‘p’ – $\pi^*(O-O)$ – can interact with another empty d-orbital (i.e. $d_{xz}$) in a $\delta$ type fashion (Fig. 10). In fact, the calculated molecular orbitals suggest that the anti-bonding combinations of the above mentioned $\delta$- and $\pi$-bonds are the LUMO and LUMO+1 of the MTO bisperoxide, respectively.

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perpendicularly to a low-lying $\sigma^*(O-O)$ orbital. As observed for
the CST, also the $Q_o$ values of the peroxo oxygen atoms are
rather insensitive towards replacement of the pyridine ligand by
water; the corresponding water adduct shows a $Q_o$ of $-15.0$
MHz on both oxygen atoms. These values differ more in the
monoperoxo species, where $Q_o$'s are equal to $-17.2$ and $-13.0$
MHz for the cis- and trans-oxygen in the pyridine adduct,
respectively, consistent with a more dissymmetric structure
(Table 3).

**Energetic considerations in oxygen-transfer reactions**

Transition state energy calculations were performed both for
the attack of ethylene on the oxygen pseudo-cis to the methyl
group and the oxygen pseudo-trans to it. The obtained geometries
for the bis-peroxo pyridine adducts are shown in Fig. 11
(others are given as coordinate files in the EST†).

The free energy barriers from the bis-peroxo pyridine adduct
are 34.2 kcal mol$^{-1}$ and 27.2 kcal mol$^{-1}$ for transfer of the cis
and trans oxygens, respectively. Notably, the more deshielded
oxygen atom (pseudo-cis to the methyl ligand) is associated with
a less favorable oxygen transfer step, consistent with a CST
already close to what is observed in metal-oxo species, showing
the connection between reactant and product. While in H$_2$O$_2$
the dihedral angle (H–O–O–H) is calculated to be 114° with the
two LP 'p' on the oxygen pointing away from each other, the
lone pairs are coplanar in a peroxo metal complex, introducing
again a maximized $\pi$-effect (similar to DMDO and mCPBA). In
order to understand and quantify the effect of the LP 'p' back-
donation into the olefin $\pi^*$-orbital to the transition state energy,
and hence probe the importance of the $\pi$-effect, a transition state
(2nd order saddle point), where the attacking olefin is coplanar
with the peroxo O–Re–O plane was calculated for the case of the oxygen pseudo-trans to the methyl group. The ob-
tained free energy of activation was found to be at
31.6 kcal mol$^{-1}$ and thus 4.4 kcal mol$^{-1}$ higher in energy than
for the perpendicular transition state. This is consistent with
what has been found for the epoxidation with non-metal-based
peroxides, again evidencing the importance of the back-
donation of a high-lying LP 'p' on oxygen – the filled $\pi^*(O-O)$
orbital – into the olefin $\pi^*(C=C)$ orbital.

Similar trends are observed for the bis-peroxo water adduct
with free energy barriers of 34.3 and 27.8 kcal mol$^{-1}$, for the
transfer of the cis- and trans-oxygen, respectively. For the monoperoxo intermediate, the free energy barriers for O-transfer are
typically slightly higher (>29.0 kcal mol$^{-1}$) for both oxygen
atoms, at the exception of the cis-peroxo oxygen of the pyridine
adduct (26.8 kcal mol$^{-1}$). These results suggest that the bis-
peroxo complex is possibly the more reactive species in water,
and that in the presence of pyridine both mono- and bis-peroxo
complexes are reactive.$^{72,73}$ Thus pyridine may have a dual role,
*i.e.* as a phase transfer agent and as a ligand to accelerate
catalysis.$^{17,76}$ Notably, for all metal-peroxo compounds, the
easier oxygen transfer is associated with the peroxo oxygen with
smaller $\delta$ and $\delta_1$, while the oxygen atom which is not trans-
ferred displays a larger oxo-character, evidenced by the larger
$\delta$ and $\delta_1$.

As for DMDO and mCPBA, the coplanarity of the two oxygen
lone pairs LP 'p' in the MTO peroxo species maximizes the $\pi$
-effect, raising the energy of the lone pairs thereby increasing
their reactivity. In addition, the $\pi$-interaction of the peroxo
moiety with the metal (Fig. 10) assists the oxygen transfer
process in olefin epoxidation, during which a fully developed
$\pi$(Re=O) bond is formed.

Notably, the spectator oxo-ligand in the apical position in the
bisperoxo Re complex is not innocent: this oxo-ligand interacts
with the peroxo moiety *via* the metal d-orbitals involved in the
$\pi$- and $\delta$-interactions (Fig. 10). This interaction minimizes
the stabilization of the peroxo LP 'p' by weakening the (stabilizing)
$\delta$- and $\pi$-bonds. In addition, the presence of the spectator oxo-
ligand also provides a driving force for the formation of the metal-peroxo species in the catalytic cycle: formation of the
peroxo species from MTO strengthens the bond of the apical
“spectator” oxo-ligand as evidenced by a slight decrease of the
Re=O bond length on going from MTO (1.69 Å) to the
monoperoxo (1.68 Å) and then the bisperoxo (1.67 Å) pyridine
adducts. This effect is reminiscent of the spectator oxo effect
discussed for metallacyclobutane formation from metal alkyl-
dienes during the olefin metathesis reaction, as well as for the
formation of metallacycle oxetane intermediates in the reaction
of alkenes with metal oxo compounds.$^{77-79}$

**Conclusions**

Overall, peroxide compounds are associated with significantly
deshielded $^{17}$O chemical shifts that indicate the presence of
low-lying vacant and high-lying occupied orbitals, correspond-
ing to the $\sigma^*(O-O)$ and the lone pairs on oxygen, associated
with $\pi$(O–O) and $\pi^*(O-O)$, for both metal-based and non-metal-
based peroxides. These specific electronic features are particu-
larly pronounced in peroxide species that engage in electrophilic epoxidation reactions (DMDO, mCPBA, and MTO
bisperoxo), as evidenced by their remarkably large deshielding.
This is due to the coplanarity of the oxygen lone-pairs in these
peroxides which is induced by their strained cyclic structure or
by H-bonding in the case of mCPBA. Both maximize overlaps
and in fine raises the HOMO ($\pi$-effect) and increases reactivity
towards electrophilic epoxidation. In metal peroxo species, this
HOMO is further raised in energy by the presence of a spectator oxo-ligand in the apical position. In fact, this “spectator” oxo species participates in modulating the reactivity of peroxo intermediates in transition-metal-catalyzed oxidation processes; it is thus not surprising that such a moiety is ubiquitous in efficient epoxidation catalysts that use H2O2 as a primary oxidant. The $\pi$-effect and the presence of a strained cyclic structure goes hand in hand with a weakening of the O–O bond. Both the high-lying lone pair of the cyclic structure goes hand in hand with a weakening of the O–O bond. Thus, $^{17}$O NMR chemical shift provides a powerful descriptor to pinpoint key electronic features that are decisive for reactivity in oxidation chemistry (Fig. 12).

Epilogue

The frontier orbital interactions shown in Fig. 6 highlight the following observation: while an epoxidation with DMDO or mCPBA is typically thought of as an electrophilic epoxidation, with the oxidant acting as electrophile and the olefin acting as nucleophile, these molecular orbital interactions indicate that both substrates act as nucleophiles and electrophiles by exploiting the low-lying $\pi^*(\text{O–O})$ orbital and the high-lying lone pair LP ‘p’ (O) induced by the $\alpha$-effect. This is reminiscent of synergistic effects observed in transition metal chemistry, for example in olefin complexes or in oxidative addition processes (Fig. 13a and b). Considering that olefin epoxidation with DMDO or mCPBA is isolobal to epoxidations with oxaziridines and halogenation reactions by X2 or NXS (X = Cl, Br, I), a similar orbital picture can be anticipated for these “electrophilic” additions (Fig. 13c).

Conflicts of interest

There are no conflicts to declare.

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Notes and references