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Olefin epoxidation by dioxiranes and percarboxylic acids: an analysis of activation energies calculated by a density functional method

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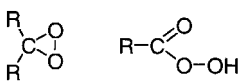
ABSTRACT: The activity of dioxiranes, R_2CO_2, and percarboxylic acids, $RCO(O_2)H$, in olefin epoxidation reactions can be rationalized by a frontier orbital interaction. Barrier heights of these oxygen transfer reactions, as calculated by a density functional method, depend linearly on the energy of the olefin HOMO orbital π (C—C) and of the peroxide LUMO orbital σ^*(O—O). Activation barriers can be predicted from linear relationships with the proton affinity of a dioxirane (as measured by the hydrogen fluoride association energy) or the pK_a value of a percarboxylic acid.

KEYWORDS: olefin epoxidation; dioxirane; percarboxylic acids; activation energies; DFT calculations

INTRODUCTION

Dioxirane derivatives[1] R_2CO_2 (**1**) and percarboxylic acids[2] $RCO(O_2)H$ (**2**) are important oxidants for the epoxidation of olefins[3] which have recently been extensively investigated by computational chemistry.[4] However, despite this wealth of computational results, some comments on the chemical reactivity of this class of compounds, their electronic structure and their Brønsted acidity/basicity still seem to be worthwhile. We will show how to estimate the heights of epoxidation barriers from easily accessible properties of the reactants. Specifically, we will correlate orbital energies and also deprotonation energies (percarboxylic acids) and proton affinities (dioxiranes) of the reactants with the calculated heights of activation barriers, and will compare them with experimentally derived reaction rates. Finally, we shall illustrate how the reactivity of percarboxylic acids can be estimated from their pK_a values.



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Organic peroxide compounds have been found to follow an electrophilic pathway when oxidizing organic substrates.[3] The influence of substituents on the reactivity of perbenzoic acids[2a] and phenylacetylenes[2b] has been studied using a Hammett analysis. In earlier experimental work, ionization potentials of olefin substrates were correlated with relative reaction rates of epoxidation reactions.[5] On the basis of an unsatisfactory correlation between ionization potentials and reaction rates, Shea and Kim excluded a frontier orbital interaction between an olefin and a peroxide as dominant factor of the reactivity.[5b] However, later, by analyzing a more consistent set of experimental data, Kim *et al.*[6] demonstrated that the epoxidation reactivity is indeed strongly affected by the HOMO–LUMO interaction, as will be corroborated by the present analysis of computational results. Kim *et al.* found separate linear relationships between the ionization potentials of olefins and log *k* of the epoxidation with *m*-chloroperbenzoic acid, depending on whether the olefins carried aliphatic and aromatic substituents.[6] They rationalized the lower reactivity of aromatic olefins with the charge delocalization due to the aromatic substituent which affects the cation radical (i.e. the ionization potential) more than the epoxidation transition state.[7]

Previously, we investigated the mechanism of olefin epoxidation by transition metal peroxo complexes[8] in a computational study and we successfully employed a frontier orbital model to rationalize differences in the epoxidation activities of such compounds.[9] In the following, we shall use this model to correlate calculated barrier heights of oxygen transfer (via direct attack of an olefin on a peroxy group) with the energies of the pertinent orbitals, the π(C—C) HOMO of the olefin and the σ^*(O—O) LUMO of the peroxy group.

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Table 1. Calculated activation barriers[a] $\Delta E^{\neq}$ (kcal mol^{-1}) for the epoxidation of olefins by various oxidants

Oxidant	Olefin	$\Delta E^{\neq}$
H_2CO_2 (**1a**)	Ethylene	13.52
	Propene	11.19
	cis-2-Butene	8.84
	2-Methyl-2-butene	7.83
	2,3-Dimethyl-2-butene	6.86
$(CH_3)_2CO_2$ (**1b**)	Ethylene	18.12
$(OH)_2CO_2$ (**1c**)	Ethylene	6.84
F_2CO_2 (**1d**)	Ethylene	−1.03[b]
$(CF_3)_2CO_2$ (**1e**)	Ethylene	3.75
Cl_2CO_2 (**1f**)	Ethylene	0.93
$HCO(O_2)H$ (**2a**)	Ethylene	14.89
$CH_3CO(O_2)H$ (**2b**)	Ethylene	17.06
	Propene	14.73
	cis-2-Butene	12.33
	2-Methyl-2-butene	11.02
	2,3-Dimethyl-2-butene	9.69
$HOCO(O_2)H$ (**2c**)	Ethylene	14.65
$FCO(O_2)H$ (**2d**)	Ethylene	11.12
$CF_3CO(O_2)H$ (**2e**)	Ethylene	10.62
$ClCO(O_2)H$ (**2f**)	Ethylene	9.69

[a] Differences between the energies of the transition state and the sum of the energies of the reactants, without further corrections.
[b] Negative value due to the basis set superposition error.

The present discussion will be based on computational results[10] obtained with the hybrid B3LYP density functional approach.[11] Whereas the study of Kim *et al.*[6] dealt exclusively with reactivity variations of different olefins, we will focus here on the analysis of variations with different oxygen donors, but we will also briefly comment on reactivity differences among various olefins. Geometries were optimized without symmetry constraints employing a 6–311G(d,p) basis set.[12] As substrates we chose several dioxirane derivatives, R_2CO_2 (**1**) and percarboxylic acids $RCO(O_2)H$ (**2**), with functional groups R = H (**a**), CH_3 (**b**), OH (**c**), F (**d**), CF_3 (**e**) and Cl (**f**). In Table 1 we give the heights of the activation barriers for all olefin epoxidation reactions calculated in this work.

RESULTS AND DISCUSSION

In Fig. 1 we sketch the transition structures for the epoxidation of ethylene with the two prototypical systems **1b** and **2b**. In both cases the O—O bond of the oxidant is elongated: from 1.500 Å in **1b** to 1.893 Å in the epoxidation transition state and from 1.439 Å in **2b** to 1.873 Å in the corresponding transition state. Additionally, we note that in the transition state the C—O bond of **1b** to be broken is strongly elongated (from 1.400 to 1.516 Å), while the remaining C—O distance of **1b** is shortened to 1.316 Å on its way to a C—O double bond. Since the transition structures of other systems investigated here are similar and have also been discussed previously,[4] we refrain from further analysis.

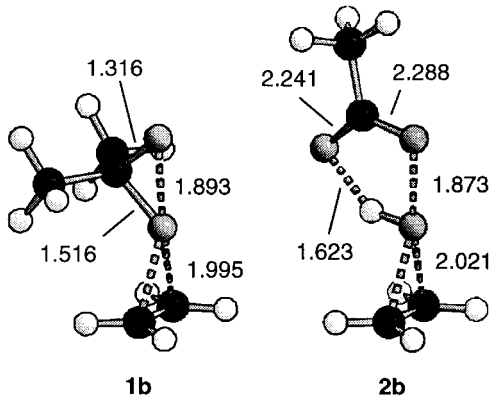

Figure 1. Transition state structures of ethylene epoxidation with compounds $(CH_3)_2CO_2$ (**1b**) and $(CH_3)CO(OOH)$ (**2b**). Bond lengths in Å

To confirm the relevance of the frontier orbital interaction, we first analyze calculated epoxidation transition states (all of them of spiro structure) of the model olefins ethylene, propene, *cis*-2-butene, 2-methyl-2-butene and 2,3-dimethyl-2-butene with the peroxide compounds **1a** and **2b**. The height of the epoxidation barrier varies linearly with the energy of the olefin HOMO (Fig. 2), just as previously found for the transition metal complexes as oxygen donors.[9] Each methyl substituent of the olefin moiety pushes more electron density into the π bond and thus raises the HOMO energy, i.e. the olefin becomes more nucleophilic.[3] Concomitantly, the energy gap between the olefin HOMO and the peroxide LUMO decreases (for a discussion of the chemical interpretation of Kohn–Sham orbital energies, see Ref. 13), entailing a lower activation barrier for epoxidation.

To compare the present analysis of computational results with experiment, we use two sets of reaction rates for the epoxidation of some of the probe olefins used here with peracetic acid **2b**. One set[14] comprises relative

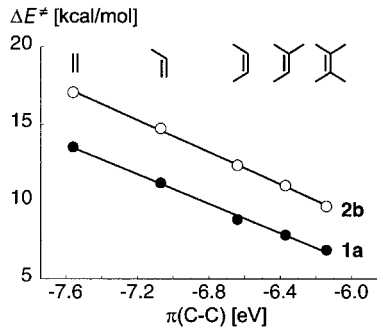

Figure 2. Calculated activation barriers $\Delta E^{\neq}$ (in kcal mol^{-1}) of epoxidation of various substituted olefins by dioxirane (**1a**) and acetic percarboxylic acid (**2b**) as function of the energy of the olefin HOMO π(C—C)

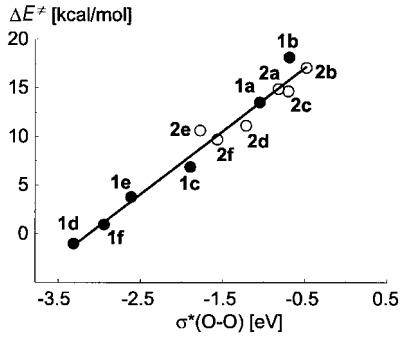

Figure 3. Calculated activation barrier $\Delta E^{\neq}$ (kcal mol^{-1}) of ethylene epoxidation by dioxiranes **1a–f** and percarboxylic acids **2a–f** as a function of the energy of the LUMO σ^*(O—O) of the oxidant

reaction rates for ethylene (0.045), propene (1.0-reference), *cis*-2-butene (22) and 2-methyl-2-butene (230); the other[5a] contains relative values for propene (1.0), *cis*-2-butene (22.1), 2-methyl-2-butene (264.3) and 2,3-dimethyl-2-butene (2643). Not surprisingly, the logarithms of these relative reaction rates correlate very well with our calculated activation barriers ($R^2 = 0.99$), corroborating the present analysis of computational results.

It is interesting that such a linear relationship holds not only for olefin epoxidation, but also for the oxidation of other substrates, e.g. the activation of C—H bonds with cyanodioxirane $H(CN)CO_2$. In fact, by calculating the energies of the pertinent σ(C—H) orbitals of methane, ethane, propane, and isobutane (-13.70, -13.31, -12.98 and -12.69 eV, respectively) one confirms a striking linear relationship with published barriers[4c] of oxygen transfer from cyanodioxirane (35.0, 27.1, 19.8, 14.2 kcal mol^{-1}, respectively, for the various substrates) (1 kcal = 4.184 kJ).

We now turn to a discussion of different oxidants. In order to evaluate the effect of different substituents R of the organic peroxy compounds on the energy of the σ^*(O—O) LUMO The σ^*(O–O) orbital is in fact always the LUMO, at variance with the electronic structure of transition metal complexes where orbitals with significant σ^*(O–O) contribution lie slightly above the LUMO that exhibits a dominating d-orbital contribution of the metal center[9] and thus on their reactivity, we calculated the barriers for the direct attack of ethylene on the peroxy groups of the compounds **1/2a–f**. Also here, a convincing linear relationship between the activation barrier and the energy of the σ^*(O—O) LUMO is obtained (Fig. 3), at variance with previous findings for the rhenium compounds $CH_3Re(O_2)_2O{\cdot}L$.[9] Obviously, substitution of different Lewis-base ligands L changes the electronic structure of the transition metal bisperoxo complexes in a more complex way than inducing merely a shift of the pertinent σ^*(O—O) orbital. In the case of organic peroxy compounds, the interaction of the substituents R with the active site of the molecule is simpler, leading to a linear relationship as expected from a perturbation theory argument: the more substituent R is able to reduce the electron density of the peroxide moiety, the stronger is the stabilization of the σ^*(O—O) orbital and the more electrophilic is the oxygen center. In this way, the HOMO–LUMO energy gap is again reduced and so is the activation barrier. Note that the calculated reaction barriers cover a wide energy range of about 20 kcal mol^{-1} (Fig. 3).

Hence the reactivity variation of the compounds R_2CO_2 and $RCO(O_2)H$ can be rationalized by the HOMO–LUMO interaction. The energy of the σ^*(O—O) orbital is a key characteristic of the electronic structure of an O—O moiety for rationalizing the activation barrier of olefin epoxidation.

Interestingly, the activation energies of percarboxylic acid derivatives **2a–f** form a more compact group in Fig. 3 and they tend to be larger than the barrier heights of the dioxiranes **1a–f**. This finding becomes quite obvious if one recalls that compounds **1a–f** feature two potential electron-withdrawing groups R, whereas compounds **2a–f** exhibit only one such substituent. Therefore, the σ^*(O—O) orbital of percarboxylic acids is stabilized less than that of the corresponding dioxiranes. Additionally, there might also be a delocalization effect in **2c**, **d** and **f** since in this case a π interaction with the sp^2 carbon center of the percarboxylic acid will be possible. However, dioxiranes and percarboxylic acids with the less electronegative substituents H and CH_3 have similar values of orbital energies and activation barriers.

It is worth noting that the linear correlation of the data displayed in Fig. 3 is much better for dioxiranes ($r^2 = 0.98$) than for percarboxylic acids ($r^2 = 0.89$). The larger mean deviation for percarboxylic acids is in part due to the proton-accepting oxygen center. Variation of the substituent R affects the basicity of the proton acceptor group hardly in the same way as the energy of the σ^*(O—O) orbital and thus creates 'noise' in the correlation.

The LUMO energy as key quantity is not easily accessible by experiment. However, the foregoing analysis can be rendered a practical tool for predicting the epoxidation reactivity from ground-state properties of the oxygen donor by realizing that the LUMO energy is expected to correlate with the acidity of a percarboxylic acid (or with the basicity of a dioxirane). The stronger the electron-withdrawing power of the substituents R, the lower is the electron density on the peroxy group and, subsequently, the lower is the deprotonation energy of a percarboxylic acid or the proton affinity of a dioxirane. Therefore, the acidity (basicity) of the oxygen source is expected to provide a direct measure of its reactivity that is preferable to the orbital energies. In the following, we will demonstrate the validity of this concept for olefin epoxidation by the percarboxylic acids **2a–f** and the dioxiranes **1a–f**.

The calculated barrier heights of epoxidation by the

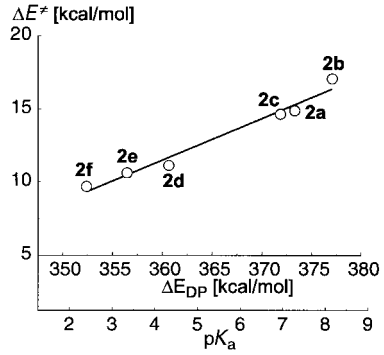

Figure 4. Activation energies $\Delta E^{\neq}$ (kcal mol^{-1}) of ethylene epoxidation by percarboxylic acids as a function of the deprotonation energies ΔE_{DP} (kcal mol^{-1}) and estimated pK_a values of the corresponding percarboxylic acids

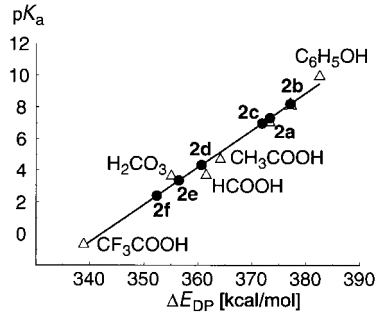

Figure 6. Experimental pK_a values as a function of calculated gas-phase deprotonation energies ΔE_{DP} (kcal mol^{-1}) of various acidic compounds (triangles). Also shown is the regression line $pK_a = 0.234\Delta E_{DP}$(kcal mol^{-1}) -80.1. Estimated pK_a values of the percarboxylic acids **2a–f** are given as filled circles

percarboxylic acids **2a–f** exhibit the expected linear variation with the deprotonation energies ΔE_{DP} in the gas phase ($AH \rightarrow A^- + H^+$); see Fig. 4. The correlation of these two quantities is even better ($r^2 = 0.97$) than that with the σ^*(O—O) orbital energies (Fig. 3). As mentioned above, this is due to the fact that proton transfer also affects the activation barrier: more acidic percarboxylic acids are found to feature lower epoxidation barriers, in agreement with experiment.[2a]

To check the dependence of the epoxidation barrier on the basicity of the dioxiranes, we calculated the proton affinity ΔE_{PA} of the peroxy group. Simple addition of a proton causes an opening of the dioxirane ring of **1c, d** and **f**, whereas for the weaker acid H_3O^+ only **1c** opens. To prevent this undesirable reaction pattern, we used hydrogen fluoride, HF (p$K_a = 3.2$),[15a] to probe the proton-accepting ability of the dioxiranes: $R_2CO_2 + HF \rightarrow R_2CO_2 \cdot HF$. The activation energies for epoxidation by dioxiranes show the expected linear correlation with the energy of HF addition (Fig. 5).

Unfortunately, strong solvent effects on the epoxidation barriers prevent a direct comparison of computational and experimental results.[16,17] Depending on the solvent, measured activation energies for cyclohexene epoxidation by **1b** vary between 4.96 ± 0.3 kcal mol^{-1} in

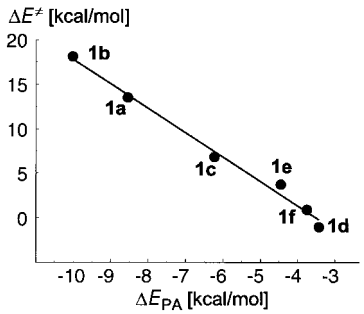

Figure 5. Activation energies $\Delta E^{\neq}$ (kcal mol^{-1}) of ethylene epoxidation by dioxiranes as a function of the proton affinity ΔE_{PA} (kcal mol^{-1}) approximated by the calculated energy of HF addition

$CDCl_3$ and 7.65 ± 0.4 kcal mol^{-1} in CH_3COOH,[16] while we estimate it to be 13.5 kcal mol^{-1} using results of this work. For the epoxidation of isobutene and α-methylstyrene by **1b** we estimate activation barriers of 13.5 and 11.7 kcal mol^{-1}, respectively; the corresponding experimental values are 9.3 ± 0.2 and 10.2 ± 0.1 kcal mol^{-1}[14f] For α-methylstyrene our estimate based on ethylene epoxidation may predict an activation barrier that is systematically too low since the effect of electron delocalization affects the orbital energies and the epoxidation barrier to different extents.[6] For isobutene, a calculated barrier of 15.3 kcal mol^{-1} has been reported;[4f] our lower estimate takes mainly electronic effects into account, but neglects steric interactions between substituents. These deviations between computational and experimental results are large and appear to be systematic. In a separate study,[17] we showed that solvent effects lower activation barriers by 4–8 kcal mol^{-1}, bringing estimated and calculated barriers heights into better agreement.

Finally, to relate gas-phase deprotonation energies to a more commonly used experimental quantity, we point out that the deprotonation energy ΔE_{DP} can be linked to the acid-proton dissociation energy in aqueous solution. In fact, ΔE_{DP} varies linearly with the (experimental) pK_a value of the percarboxylic acid (Fig. 6). pK_a values are difficult to determine computationally. However, if we assume that all corrections which have to be applied to the gas-phase value ΔE_{DP}, such as solvent effects and vibrational energy corrections, can be accounted for by simply fitting to a database, then we find the expected linear relationship between calculated ΔE_{DP} and measured pK_a values[15] (Fig. 6). In our database we included experimental pK_a values of compounds **2a** (7.1) and **2b** (8.2)[15b] and of some organic and inorganic compounds (Fig. 6). Via a second x-axis in Fig. 5 we display how the activation barriers of percarboxylic acids depend on the estimated pK_a values.

CONCLUSION

The (calculated) barrier heights of olefin epoxidation by dioxiranes or percarboxylic acids can be rationalized by reference to properties of the oxygen donors which may, at least in principle, be obtained from experiment: the energies of HF association as measure of the basicity of dioxiranes and the pK_a values or deprotonation energies as measure of the acidity of percarboxylic acids.

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