Solvent Effects on the Activation Barriers of Olefin Epoxidation − A Density Functional Study

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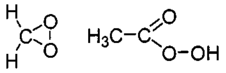
Solvent effects reduce the activation energies calculated for olefin epoxidation by dioxiranes and percarboxylic acids in the gas phase. Association of a proton donor to the oxygen atom of the peroxo group not attacked by the olefin activates the peroxo group and lowers the reaction barrier by 2–6 kcal/mol, in agreement with experimental findings. A polarizable solvent reduces the activation barrier further by about 2 kcal/mol. Overall, satisfactory agreement with experimental activation energies is achieved if calculated intrinsic (electronic) barriers are corrected for both types of solvent effects. As an application we also discuss the electrostatic solvent effect on the activation barrier of the olefin epoxidation by different base adducts of a rhenium bisperoxo complex and we rationalize opposite trends with different solvent dielectric constants.

Introduction

Dioxirane derivatives[1,2] R_2CO_2 (**1**) and percarboxylic acids[3−5] $RCO(O_2)H$ (**2**) (Scheme 1) are important oxidants for the epoxidation of olefins.[6,7] Such epoxidation reactions have been extensively investigated by computational methods.[8−14] Recently we reported[15] that calculated activation barriers in the gas phase correlate in a linear fashion with the energy gap between the olefin HOMO π(C−C) and the LUMO σ^*(O−O) of the epoxidizing peroxo group, as found previously also for epoxidation by transition metal peroxo complexes.[16−19]



1 **2**

Scheme 1

Activation energies are often calculated to be rather higher than the measured epoxidation barriers, as exemplified by the epoxidation of isobutene or α-methylstyrene by dimethyldioxirane (DMDO). Experimental values for these epoxidations in acetone are 9.3 ± 0.2 and 10.2 ± 0.1 kcal/mol, respectively, while the epoxidation barrier of isobutene has also been calculated to be 15.3 kcal/mol by a DFT-based method.[13] This computational result is noteworthy since barrier heights calculated with density functional methods are known to often underestimate reaction barriers.[20] From our DFT-based frontier orbital model[15] we estimate the intrinsic activation barriers of isobutene and α-methylstyrene to be 13.5 and 11.7 kcal/mol, respectively. These estimates (for isobutene lower than the calculated barrier[13] mentioned above) take electronic effects into account, but neglect steric interactions between substituents and the olefin or among the substituents R. In any case, these discrepancies between measured barriers on the one hand and calculated or estimated activation energies on the other call for further clarification. For this purpose, we shall analyze here the influence of the solvent on the activation barrier of the epoxidation reaction with the help of model calculations.

Measurements of epoxidation barriers reveal that activation energies are quite strongly affected by solvent effects,[21] as for instance demonstrated, albeit in a somewhat indirect fashion, for the epoxidation rates of *trans*-ethyl cinnamate and cyclohexene with DMDO. Since DMDO was available only in acetone solution, the experiments were performed in a 1:1 mixture of the solvent of interest and acetone.[21] With an empirical multi-parameter model that incorporates solvent properties such as proton donor (PD) and proton acceptor (PA) capacities, relative reactivity indices of 7.5 and 3.2 were derived for cyclohexene epoxidation with DMDO in acetic acid and $CDCl_3$, respectively, using acetone as reference solvent.[21] Interestingly, the corresponding activation enthalpies show the opposite trend (5.0 ± 0.3 kcal/mol in $CDCl_3$, 7.7 ± 0.4 kcal/mol in CH_3COOH), while the activation free energies are almost identical (16.9 ± 0.3 kcal/mol in $CDCl_3$ and 16.6 ± 0.5 kcal/mol in CH_3COOH), indicating large entropy effects. These studies show that solvents with PD capacity increase the reaction rate, while solvents with PA capacity decrease epoxidation rates.[21] Our frontier-orbital model[15] gives the epoxidation barrier of cyclohexene with DMDO to be 13.7 kcal/mol, again an overestimation.

In the present computational study we will analyze how the barrier heights of oxygen transfer (by direct attack of an olefin on a peroxo group) depend on the continuum properties of the solvent and on the proton-donating power of an additional agent. We will focus on dioxirane H_2CO_2 (**1**) and acetic percarboxylic acid $CH_3CO(O_2)H$ (**2**) as representative of these two classes of peroxo compounds.

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Models and Methods

The two main effects of a solvent on a molecular system are often discriminated:[22,23] a long-range electrostatic interaction, where the environment is described as a polarizable continuum, and a short-range (chemical) interaction of the solute with solvent molecules. Commonly the first effect on a molecular system is computationally analyzed within so-called polarizable continuum models (PCM) where the solute is placed in a cavity of a polarizable dielectric medium,[22,23] allowing the charge distribution of the solute to polarize the dielectric and vice versa. Such a model approach ignores the molecular structure of the solvent. On the other hand, modeling chemical interactions between solvent and solute, such as solvolysis, protonation/deprotonation, or polarization due to association of a solvent molecule (e.g. hydrogen bonds) requires explicit calculations of such effects.

In experiment it is difficult — if not impossible — to differentiate between both types of solvent effects. In the present study we shall separately model each kind of solvent effect on the olefin epoxidation by dioxiranes and percarboxylic acids. For this purpose, we will first study adducts of various proton donors at the "free" (second) oxygen center of an epoxidizing peroxo group which is not attacked by the olefin (see Figure 1). Secondly, the activation barrier of the reactions in relevant dielectric media of different polarizability will be determined.

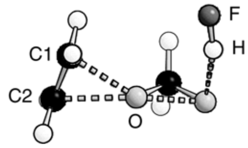

Figure 1. Optimized transition state structure of ethylene epoxidation by dioxirane associated with HF, **1**·HF

We have calculated the epoxidation barriers with ethylene as the model olefin, using the B3LYP hybrid[24,25] density functional approach.[26] Geometries were optimized without symmetry constraints using a 6−311G(d,p) basis set.[27,28] Long-range electrostatic solvent effects were treated with the IEFPCM method (integral equation formalism, polarized continuum model).[29]

To model the effects of a chemically interacting protic solvent (i.e. the PD capacity of the solvent),[21] we determined the epoxidation barriers for adducts **1**·HA with a proton donor associated at the dioxirane oxygen center not attacked by the olefin (Figure 1). We investigated various Brønsted acids HA (H_2O, H_2S, HF, and HCl); see Figure 1 for the transition state structure of ethylene epoxidation by the adduct **1**·HF. Obviously, in "real" systems, the interactions of solute and solvent are much more complicated than those depicted in such a simple model approach. Indeed there may be more than only one proton donor associated to the peroxo compound. Additionally, we refrained from extensive checks to assure that the optimized starting structures are global minima on the potential energy surface of the adduct **1**·HA. This restriction is in the spirit of the present model study which aims at elucidating trends rather than at quantifying such short-range solvent effects. In fact, we do not expect that there are other structures with considerably different energetics since the calculations were performed without symmetry restriction. To achieve quantitative results, ab initio molecular dynamics calculations are required, a modeling approach that is computationally much more demanding and certainly beyond the scope of the present exploratory model study.

Results and Discussion

Table 1 presents the association energies ΔE_{HA} of the adduct systems **1**·HA and the corresponding activation barriers $\Delta E^{\ddagger}$ for the epoxidation reaction of ethylene. Also listed are the pK_a values[30] of the proton donors HA. In clear agreement with experimental results,[21] we obtain an increased reactivity of the system due to the association of proton donors. The activation barriers drop with increasing acidity of HA from 13.5 kcal/mol for dioxirane in the gas phase to about 7.2 kcal/mol for HF as proton donor; a further increase of the acidity of the proton donor does not seem to decrease the barrier beyond this value.

Table 1. Calculated association energies ΔE_{HA} of various proton donors HA to dioxirane **1** and the corresponding ethylene epoxidation activation energies $\Delta E^{\ddagger}$ of the adducts **1**·HA; energies in kcal/mol; also given is the experimental pK_a value of HA.

HA	pK_a [a]	ΔE_{HA}	$\Delta E^{\ddagger}$
None	–	–	13.52
H_2O	15.7	−7.36	11.26
H_2S	7	−2.86	10.28
HF	3.2	−8.54	7.23
HCl	−8	−4.89	7.27

[a] See ref.[30].

Long-range electrostatic solvent effects[29] on the activation barriers of the three systems **1**, **1**·HF, and **2** were determined for various solvents (dielectric constant ε in parentheses): C_7H_{16} (1.9), CCl_4 (2.2), $CHCl_3$ (4.9), CH_2Cl_2 (8.9) CH_2ClCH_2Cl (10.4), $(CH_3)_2CO$ (20.7), CH_3CN (36.6), $(CH_3)_2SO$ (46.7).[31]

To represent the results for a system X in compact form we resorted to the Onsager reaction field model.[22] In a spherical cavity of radius $a(X)$, a system with dipole moment $\mu(X)$ undergoes a stabilization ΔE_{sol} when interacting with a surrounding medium of dielectric constant ε:

$$\Delta E_{sol}(\varepsilon,X) = -(1-3/(2\varepsilon+1))\,\mu^2/2a^3 = -\kappa(\varepsilon)\,\eta_m(\mu,a) \tag{1}$$

In this simple model, back-polarization of the solute on the solvent is neglected. The scaling factor $\kappa(\varepsilon) = 1 - 3/(2\varepsilon + 1)$ characterizes the solvent; it varies from $\kappa = 0$ for the gas phase ($\varepsilon = 1$) to $\kappa = 1$ for $\varepsilon \to \infty$. This limit is almost reached for water as solvent, $\kappa(\varepsilon) = 0.98$. The system dependent quantity $\eta(X)$ characterizes the polarity of the solute X, i.e. its sensitivity to the polarizing capacity of the medium; it represents the maximum value of the solvent effect on the total energy achievable due to embedding in a dielectric environment. Later on, we will use the scaling relationship in Equation (1) with the proportionality constant $\kappa(\varepsilon)$ to determine $\eta(X)$ from accurate IEFPCM results [see Equation (3)]. From the Onsager model [Equation (1)], with a spherical cavity of volume $V(X)$ we obtain the model approximation $\eta_m(X)$:

$$\eta_m(X) = \mu(X)^2 / 2a(X)^3 = (2\pi/3)\mu(X)^2 / V(X) \tag{2}$$

In Table 2, we present the computed solvent effects $\Delta E_{sol}(\varepsilon)$ on the total energy of the systems of interest (oxidants, ethylene, and the corresponding transition states) by quoting the quantity $\eta(X)$ fitted to the B3LYP-IEFPCM results $E_{tot}(\varepsilon,X)$ in various solvents:

$$\Delta E_{sol}(\varepsilon,X) = E_{tot}(\varepsilon,X) - E_{tot}(1,X) = -\kappa(\varepsilon)\eta(X) \tag{3}$$

Table 2. Coefficient η [in kcal/mol, see Equation (3)], dipole moment μ (in Debye) and volume V of the Onsager cavity (in Å^3) for ethylene, **1**, **1**·HF, **2**, and various rhenium bisperoxo base adducts **3**·L [L = H_2O, pyridine (py), pyrazole (pz)] from B3LYP−IEFPCM calculations; also shown are these characteristics for the corresponding transition states of ethylene epoxidation (marked by ‡) and the resulting sensitivity parameter $\Delta\eta^‡$ of the transition state [see Equation (4)]

	η	η‡	Δη‡	μ	μ‡	V	V‡
C_2H_4	0.30	–	–	0	–	131	–
1	3.34	5.94	2.30	2.61	4.82	76	180
1·HF	4.28	6.25	1.67	3.01	5.31	112	217
2	2.94	4.54	1.30	2.31	2.56	146	249
3·H_2O	10.10	11.65	1.25	2.74	4.25	160	236
3·py	7.19	6.95	−0.54	5.88	5.93	253	326
3·pz	9.93	9.97	−0.26	5.41	5.29	229	303

The calculated solvent effects fit this relationship perfectly; the correlation coefficients R^2 of the fit are at least 0.998. In Figure 2 we provide a graphical representation of the solvent effect for the activation barriers of ethylene epoxidation with the systems **1**, **1**·HF, and **2**; this presentation confirms the essentially linear variation of the solvent effect $\Delta E_{sol}(\varepsilon,X)$ with $\kappa(\varepsilon)$. Inspecting Table 2, we note that, as expected, in related systems η increases with the dipole moment μ of the system [see Equation (2)].

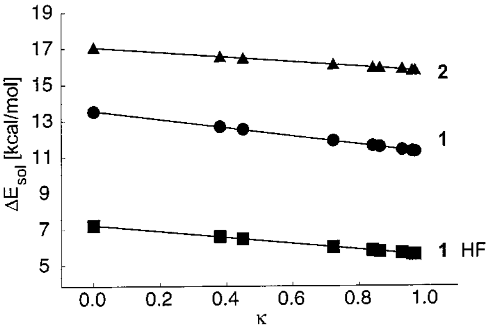

Figure 2. Calculated energy barriers $\Delta E^‡_{sol}$ (in kcal/mol) for the epoxidation of ethylene by the compounds **1**, **1**·HF and **2** as a function of $\kappa = 1 - 3/(2\varepsilon + 1)$, with ε the dielectric constant of the solvent; the media corresponding to the ε values displayed are (in order of increasing κ, given in parentheses): gas phase (0), C_7H_{16} (0.38), CCl_4 (0.44), $CHCl_3$ (0.72), CH_2Cl_2 (0.84), CH_2ClCH_2Cl (0.86), $(CH_3)_2CO$ (0.93), CH_3CN (0.96), and $(CH_3)_2SO$ (0.97)

The corresponding representation of the dielectric solvent effect $\Delta^2E^‡_{sol}$ on the epoxidation barrier $\Delta E^‡$ at transition state TS is:

$$\begin{aligned}\Delta^2E^‡{}_{sol}(\varepsilon,X) &= \Delta E_{sol}(TS) - \Delta E_{sol}(X) - \Delta E_{sol}(C_2H_4)\\ &= -\kappa(\varepsilon)[\eta(TS) - \eta(X) - \eta(C_2H_4)]\\ &= -\kappa(\varepsilon)\Delta\eta^‡(X)\end{aligned} \tag{4}$$
With $\Delta\eta^‡(X) = \eta(TS) - \eta(X) - \eta(C_2H_4)$.

Oxidant **1** exhibits the largest effect of a polarizable continuum description of the solvent on the epoxidation barrier (Table 2). The activation barrier of ethylene epoxidation in the gas phase decreases in water by $\Delta\eta^‡ = 2.3$ kcal/mol to $\Delta E^‡_{sol} = 11.2$ kcal/mol (using the data from ref. 15). For the proton donor adduct **1**·HF this sensitivity to a dielectric environment drops to $\Delta\eta^‡ = 1.7$ kcal/mol, and the limiting barrier height is rather low at 5.6 kcal/mol.[15] The lowest value, $\Delta\eta^‡ = 1.3$ kcal/mol, is found for **2** in conjunction with the highest limiting value of the activation barrier, 15.8 kcal/mol.[15] Since the values $\Delta\eta^‡$ do not differ much, the effect of the electrostatic solute−solvent interaction is quite similar in all systems and the epoxidation barriers are rather uniformly reduced by 1−2 kcal/mol. The small differences in $\Delta\eta^‡$ between the systems **1**, **1**·HF, and **2** may be rationalized by noting that the O−O bond has to be polarized for the epoxidation to proceed. Apparently, formation of a proton donor adduct reduces the polarizability of the peroxo group, fixes somehow the charge distribution in the O−O moiety, and the peroxo bond of **1**·HF is not as activated by the solute-solvent interaction as that of **1**.

Recall that the discrepancy between the calculated[13] (15.3 kcal/mol) and the experimental activation barrier (9.3 kcal/mol in acetone) for the epoxidation of isobutene by dimethyldioxirane DMDO is 6 kcal/mol.[13] Assuming small amounts of water to be present in acetone, the barrier will be reduced by about 2.3 kcal/mol by water adduct formation. The polarizing effects of acetone as dielectric environment will decrease the barrier further by about 2.1 kcal/mol. The total solvent effect by a water/acetone solvent lowers the theoretical value of the barrier to 10.9 kcal/mol. Thus, the discrepancy to the experimental value of 9.3 kcal/mol is significantly reduced when short-range and long-range solvent effects are taken into account. The remaining discrepancy between the measured and the corrected computational values may in part be due to computational parameters (the 6−31G* basis set[13] may need to be improved) and model assumptions (solvent effects were estimated for dioxirane and ethylene as model olefin).

In summary, the activation energies of olefin epoxidation are reduced due to solvent effects. On the one hand, association of a proton donor at the oxygen center of the peroxo group not directly attacked by the olefin reduces the epoxidation barrier by 2 to 6 kcal/mol (Table 1). In addition to this short-range interaction, the epoxidation barriers are lowered by about 1−2 kcal/mol due to the long-range electrostatic interaction with a polarizable dielectric medium (Table 2).

Application

Finally, as an application of the present analysis of solvent effects, we consider the effect of the electrostatic solute−solvent interaction on the activation energies of olefin epoxidation by methyltrioxorhenium with hydrogen peroxide, CH_3ReO_3/H_2O_2. Detailed computational results on these epoxidation systems have been described elsewhere.[16−18,32] The calculated gas-phase barriers for the direct attack of C_2H_4, analogous to the epoxidation pathway of organic peroxo compounds (see Figure 1),[8−14] on $CH_3Re(O_2)_2O{\cdot}L$ (**3**·L) are 16.2, 15.9, and 14.9 kcal/mol for L = H_2O, pyridine (py), and pyrazole (pz), respectively. In Figure 3 we present the calculated reaction barriers of **3**·L for three different environments: gas phase (ε = 1), toluene (ε = 2.4), and water (ε = 78.4). While in the gas phase, the water ligated Re complex exhibits the highest barrier, the pyridine stabilized analogue shows a larger activation barrier already in toluene as solvent. For water as solvent, we find the complex **3**·H_2O to feature the smallest epoxidation barrier, 15.4 kcal/mol (Figure 3). The solvent effect on the reaction barrier of **3**·H_2O is in line with that of the organic peroxo compounds discussed above; however, the reaction barriers for pyridine and pyrazole as base ligands increase with the polarity of the solvent, e.g. in the commonly used solvent CH_2Cl_2 (ε = 8.93, κ = 0.84).

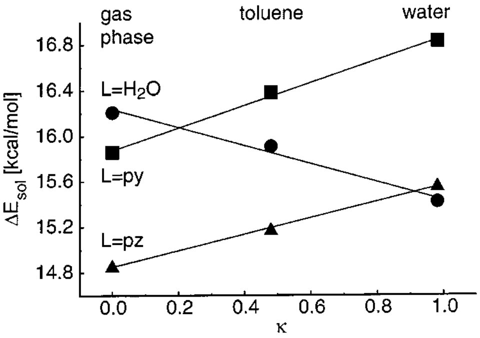

Figure 3. Calculated solvent effect $\Delta^2 E^{\ddagger}_{sol}$ (in kcal/mol) on the energy barriers for the epoxidation of ethylene by various rhenium bisperoxo base adducts $CH_3Re(O_2)_2O{\cdot}L$ [L = H_2O, pyridine (py), pyrazole (pz)] as a function of $\kappa(\varepsilon) = 1 - 3/(2\varepsilon + 1)$, with ε the dielectric constant of the solvent

These differences in the solvent effect $\Delta E^{\ddagger}_{sol}$ of the epoxidation barriers of ethylene may be rationalized by expanding the model quantity $\Delta\eta^{\ddagger}_{m}$ [see Equations (2) and (4)] to first-order:

$$\Delta^2 E^{\ddagger}_{sol}(\varepsilon,X) \approx \kappa(\varepsilon)(-2\Delta\mu/\mu + \Delta V/V)\eta_m(X) \tag{5}$$

Here, we have introduced the difference $\Delta\mu(X)$ between the dipole moment of the transition state of a system X and the corresponding ground state, as well as the corresponding volume change $\Delta V(X)$ of the Onsager cavity; contributions due to ethylene are small (see Table 2) and have been neglected. While Equation (5) does not provide a semiquantitative estimate of the values of $\Delta\eta^{\ddagger}$ determined from the self-consistent application of the IEFPCM method, it does allow us to rationalize the different signs of **3**·L in the case of L = H_2O on the one hand and of L = py and pz on the other. First, we observe that the effect of the volume change $\Delta V(X)$ tends to increase the epoxidation barrier in all cases by a similar amount ($\Delta V/V$ = 0.47, 0.29, 0.32 for L = H_2O, pyridine, and pyrazole, respectively; cf. Table 2). In the case of pyridine and pyrazole, this is the dominating effect since $\Delta\mu/\mu$ is very small, 0.01 and −0.02, respectively. For L = H_2O, just as for the organic peroxo compounds, the large increase of the dipole in the transition state induces a reduction of the epoxidation barrier; for **3**·H_2O the corresponding value $\Delta\mu/\mu$ is 0.55 (cf. Table 2).

Previously, we had analyzed[16] the electronic effects on the barrier to ethylene epoxidation due to the formation of a base adduct **3**·L; we attributed the higher activation barriers of base adducts **3**·L to the reduced electrophilicity of the peroxo oxygen center under attack by the olefin. As a result of the present investigation of solvent effects, we note that these increases in the activation barriers due to base adduct formation can be overcompensated by this electrostatic solvent effect. Therefore, while the barriers of base adducts with pyridine and pyrazole are lower in the gas phase than the barrier of the adduct with water, this ordering may be reduced or even reversed in a solvent. In this context one should compare the calculated barrier heights of ethylene epoxidation in the gas phase to those in toluene and water as shown in Figure 3. This finding rationalizes the observation that the effect of specially designed aromatic N-base ligands, e.g. for stereoselective epoxidation,[33] can be foiled due to electrostatic solute-solvent interaction, even in such weakly polar solvents as toluene.

In conclusion, to estimate the electrostatic solvent effect of any solvent on reaction and activation energies, it suffices to interpolate the energy values from two calculations, for the gas phase and for water as solvent, using the appropriate scaling parameter $\kappa(\varepsilon)$.

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