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Are Peroxyformic Acid and Dioxirane Electrophilic or Nucleophilic Oxidants?[†,#]

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The electronic character of peroxyformic acid and dioxirane has been clarified by the analysis of donor−acceptor interactions in 16 transition states (TS) for the epoxidation of olefins. Is has been shown that the olefins are attacked by peroxyformic acid (PFA) in an electrophilic way. A relation of the electronic character to reactivity has been found: the more electrophilic the attack on the C=C bond is, the faster the reaction. In contrast, dioxirane (DO) has been identified as both an electrophilic and nucleophilic oxidant, depending on the substituents at the C=C double bond. The substrates with electron-withdrawing groups are attacked by DO in a nucleophilic way. These reactions have comparably low activation barriers. For instance, the acrylonitrile epoxidation with dioxirane is significantly faster than the corresponding reaction with PFA and proceeds via a transition state with a smaller extent of reaction and a larger extent of asymmetry.

Introduction

The unique process of alkene epoxidation has been used for many years on both an industrial scale and under laboratory conditions. Oxiranes are valuable intermediates for the synthesis of compounds with vicinal functional groups. Recent computational studies[1−3] on alkene epoxidation with oxidants such as peroxy acids and dioxiranes revealed that these reactions are concerted and proceed via a transition state with *spiro* geometry; the most recent work by Adam, Bach, and coworkers,[1o] Houk and co-workers,[2j] and Gisdakis and Rösch[1p] was carried out to illuminate the stereoselectivity of the reactions of peroxy acids and dioxiranes with selected substrates and to study solvation effects on the activation barriers of epoxidations.

Despite a considerable amount of theoretical work on these epoxidations,[1,2] little is known about whether the oxidant attacks the substrate in an electrophilic or nucleophilic way and whether there is a relation of this property, which is denoted *the electronic character of oxygen transfer*, to the reactivity. Negative ρ values from Hammett studies on the epoxidation of styrenes with dimethyldioxirane and perbenzoic acid indicated an electrophilic attack on the substrate.[4,5] The most popular probe for the electronic character of oxygen transfer is the chemoselective oxidation of thianthrene 5-oxide (SSO), introduced by Adam and co-workers (Scheme 1).[6] Electrophilic oxidants preferentially attack the molecule at its sulfide moiety while nucleophilic oxidants transform the sulfoxide moiety of SSO to the sulfone. A recent

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[†] Dedicated to Professor Dr. Gernot Frenking.

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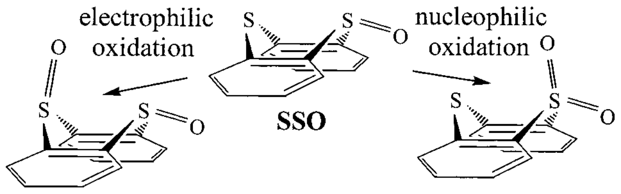
Scheme 1. Chemoselective Oxidation of Thianthrene 5-Oxide (SSO).



density-functional study[7] on SSO revealed unexpected properties of the molecule and has stimulated the development of additional probes. Very recently, Charge Decomposition Analysis (CDA), which was developed by Frenking and co-workers,[8–10] was suggested as a quantum-chemical probe: transition states (TSs) for olefin epoxidation can be analyzed in terms of donor–acceptor interactions between the olefin and oxidant fragments. The ratio of charge donation from one fragment to the other and vice versa is a measure of the electronic character.[11] The analysis of the TSs for ethylene epoxidation identified both peroxy acids and dioxiranes as electrophilic oxidants, but whether this is also true for substituted olefins has remained unclear.[11]

We present the last part of the trilogy, On the Electronic Character of Oxygen-Transfer Reactions, focusing on two goals: First, new computational results are reported in order to gain a unified view of substituent effects on the transition-state geometries and activation energies for the olefin epoxidation with peroxyformic acid (PFA) and dioxirane (DO). Second, we have investigated the electronic structure of the transition states using the recently proposed quantum-chemical probe.[11] Surprisingly, the analysis reveals a divergent electronic character of the two oxidants in the epoxidation of alkenes with electron-withdrawing groups.

Methods

For geometry optimizations, the three-parameter hybrid functional of Becke[12] together with the correlation functional of Lee, Yang, and Parr (B3LYP)[13] were employed as implemented in Gaussian 98.[14] The basis set 6-31G(d,p) was used.[15,16] Minima ($i = 0$) and transition states (TS, $i = 1$) on the potential-energy surfaces were characterized by the number i of imaginary frequencies. The energies reported are not zero-point-energy corrected. The RB3LYP solutions for all transition structures reported in this work are singlet and triplet stable.[17] For the analysis of donor–acceptor interactions in the TSs, charge decomposition analysis (CDA)[8,9] has been utilized: The Kohn–Sham MOs of each transition state are expressed as a linear combination of the MOs of the fragments olefin (*donor*) and oxidant (*acceptor*) in TS geometry. We define (i) the interaction among the occupied orbitals of ethylene and the vacant orbitals of the oxidant as donation d, (ii) the interaction among the occupied oxidant orbitals and the vacant ethylene orbitals as back-donation b, (iii) the interaction of the occupied orbitals of both fragments as repulsive polarization r, and (iv) the interaction of the vacant orbitals of both fragments as a rest term Δ. For the electronic character of oxygen transfer, the ratio d/b in the transition state is important. Oxidants with $d/b > 1$ are electrophilic while oxidants with $d/b < 1$ are nucleophilic. This quantum-chemical probe is superior to atomic partial charges.[11] The CDA calculations were performed using the program CDA 2.1.[18]

Results and Discussion

Transition Structures and Reactivity. We have calculated the geometries of the reactants, transition-states, and products for the epoxidation of 8 olefins $CH_2{=}CHR$ (R = H, CH_3, CH_2OH, $CHCH_2$, NH_2, CN, CHO) and $CH_2{=}C(CHO)_2$ with peroxyformic acid (PFA) and dioxirane (DO).[19] Selected geometrical parameters are listed in Table 1; the transition structures for ethylene and acrolein are shown in Figure 1. As the epoxidation of ethylene, the epoxidations of the other olefins are also concerted and proceed via a transition state with *spiro* geometry at the transferred oxygen. We focus on two parameters to describe the TS: the extent of reaction and the extent of asymmetry.

We find an extent of reaction ξ[20] of 0.37 for the TS of ethylene epoxidation with PFA (Table 1), indicating an early transition state on the reaction coordinate connecting the reactants ($\xi = 0$) and products ($\xi = 1$). The TSs for the reactions with electron-donating substituents are considerably earlier than the transition state for ethylene while electron-withdrawing groups shift the TS toward larger ξ values. The effects are strongest for the olefins

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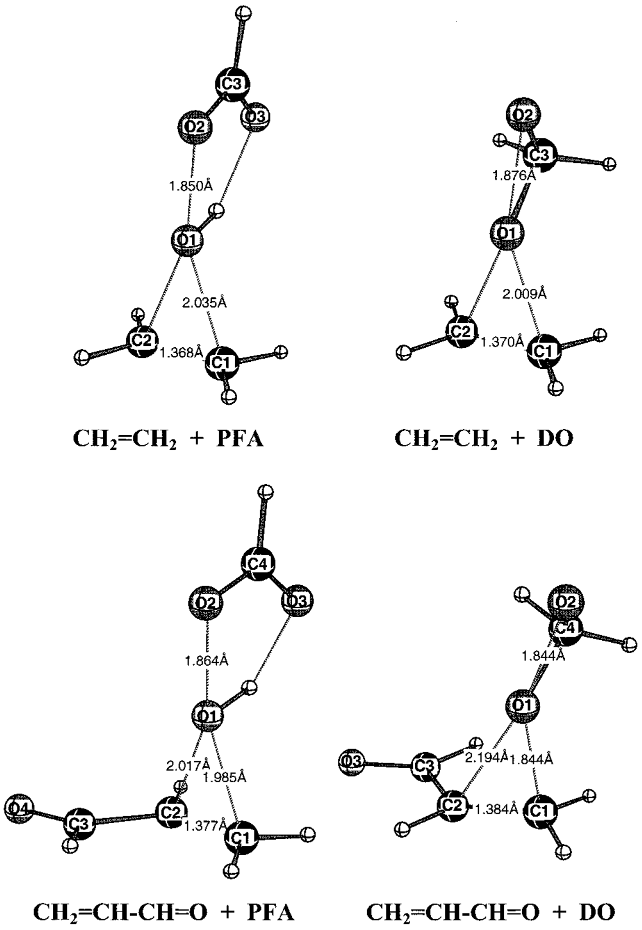
[19] Only the stereoisomers lowest in energy have been considered but the energy difference between the isomers is small and might change when improved basis sets and solvent models are employed (ref 1o). The transition state geometries that were already reported by Bach and co-workers, Houk and co-workers, and others (refs 1 and 2) at other theoretical levels have been taken from the literature and re-optimized. For the conjugated systems, the *transoid* conformation has been studied. For vinylamine, the competiting oxygen transfer to the amino moiety has not been investigated. For examples for theoretical studies on the oxidation of amines, see: (a) Bach, R. D.; McDouall, J. J. W.; Winter, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 8586. (b) Miaskiewicz, K.; Teich, N. A.; Smith, D. A. *J. Org. Chem.* **1997**, *62*, 6493.

Table 1. Selected Geometrical Parameters of the Transition States (TS), Reactants (re), and Products (pr) of Olefin Epoxidation with Peroxyformic Acid (PFA) and Dioxirane (DO), O1−(C1═C2) Distance (Å),[a] O1−C1−C2 and O1−C2−C1 Angles (deg),[b] the Extent of Reaction ξ,[c] the Extent of Asymmetry χ,[c] Calculated (B3LYP/6-31G(d,p)) Activation Energies E_a, and Reaction Energies E_r (kcal/mol)

		re[d]	pr			TS										
ox	olefin	C1−C2	C1−C2	O1−C1	O1−C2	O1−O2	C1−C2	O1−C1	O1−C2	O1−(C1═C2)	O1−C1−C2	O1−C2−C1	ξ	χ	E_a	E_r
PFA	CH_2═CH_2	1.331	1.469	1.429	1.429	1.850	1.368	2.035	2.035	1.911	70.3	70.3	0.37	0.00	14.2	−46.5
DO						1.876	1.370	2.009	2.009	1.887	70.0	70.0	0.36	0.00	13.2	−52.1
PFA	CH_2═CH(CH_3)	1.333	1.470	1.433	1.434	1.844	1.370	2.061	2.061	1.944	70.6	70.5	0.36	0.00	12.3	−48.0
DO						1.876	1.373	1.992	2.073	1.909	73.4	67.1	0.35	0.06	11.3	−53.6
PFA	CH_2═CH(CH═CH_2)	1.340	1.477	1.425	1.442	1.850	1.377	2.013	1.911	1.945	75.1	66.1	0.36	0.08	13.7	−43.8
DO						1.843	1.379	2.128	2.332	1.911	88.7	55.0	0.33	0.31	10.6	−49.4
PFA	CH_2═CH(NH_2)	1.339	1.463	1.439	1.447	1.783	1.371	2.054	2.482	2.053	90.6	55.8	0.29	0.31	5.0	−47.1
DO						1.828	1.371	2.075	2.324	2.054	82.0	62.1	0.28	0.18	4.6	−52.7
PFA	CH_2═CH(CN)	1.479	1.479	1.426	1.429	1.843	1.384	1.861	2.161	1.843	82.1	58.5	0.39	0.22	18.2	−41.7
DO						1.821	1.388	1.799	2.282	1.799	90.5	52.0	0.36	0.35	14.5	−47.3
PFA	CH_2═CH(CHO)	1.338	1.482	1.419	1.436	1.864	1.377	1.985	2.017	1.877	71.1	68.7	0.39	0.02	17.7	−43.7
DO						1.844	1.384	1.844	2.194	1.834	84.3	56.7	0.40	0.25	15.1	−49.3
PFA	CH_2═C$(CHO)_2$	1.343	1.493	1.409	1.440	1.853	1.382	1.959	2.033	1.869	72.6	66.8	0.39	0.05	19.8	−40.9
DO						1.817	1.392	1.820	2.197	1.813	85.1	55.6	0.35	0.27	12.9	−46.5
PFA	CH_2═CH(CH_2OH)	1.332	1.467	1.443	1.438	1.820	1.366	2.126	2.088	1.991	69.5	72.5	0.33	−0.03	7.9	−50.3
DO						1.867	1.371	2.092	1.993	1.918	66.5	74.3	0.34	−0.07	8.3	−55.8

[a] Distance between the O1 atom and the C1═C2 moiety. [b] The terminal carbon atom is denoted C1. [c] For the definition of ξ and χ, see footnotes 20 and 21. [d] O1−O2 distances in the free oxidants: 1.444 Å (PFA), 1.505 Å (DO).



CH_2=CH_2 + PFA CH_2=CH_2 + DO

CH_2=CH-CH=O + PFA CH_2=CH-CH=O + DO

Figure 1. Optimized transition-state geometries (B3LYP/6-31G(d,p)) for the epoxidation of ethylene and acrolein with peroxyformic acid (PFA) and dioxirane (DO).

with donor and acceptor substituents in conjugation with the C═C bond, such as vinylamine (ξ = 0.28) and acrylonitrile (ξ = 0.39). The extent of reaction at the transition states for the olefin epoxidations with DO is very similar for most of the substrates but, surprisingly, some of the TSs with electron-withdrawing groups, e.g. acrylonitrile, are as early on the reaction coordinate as the TS for ethylene epoxidation (ξ = 0.36, Table 1).

We have also determined the extent of asymmetry χ in the transition states.[21] The TS geometry for ethylene epoxidation with PFA is symmetric (χ = 0), i.e., the formation of both oxygen−carbon bonds is synchronous.

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(20) The extent of reaction ξ in the transition states has been defined as follows:

$$\xi = [d(\mathrm{O1-O2,TS}) - d(\mathrm{O1-O2,re})]/[d(\mathrm{O1-O2,TS}) - d(\mathrm{O1-O2,re}) + d(\mathrm{O1-(C1{=}C2),TS}) - d(\mathrm{O1-(C1{=}C2),pr})]$$

O1 is the proximal oxygen atom, which is transferred, while O2 is the distal oxygen (Figure 1). C1 is the terminal carbon atom of the C═C bond and C2 is the vicinal carbon atom. The d(O1−O2) values are the O1−O2 distances in the transition states (TS) and in the reactants (re), respectively. d(O1−(C1═C2)) is the minimum distance between the O1 atom and the C═C bond in the TS and in the product (pr), respectively.

(21) The extent of asymmetry χ in the transition states has been defined as follows:

$$\chi = \frac{d(\mathrm{O1-C1,TS}) - d(\mathrm{O1-C2,TS})}{d(\mathrm{C1-C2,TS})}$$

The d(X−Y) values are the distances between the atoms X and Y in the transition states (Figure 1). The difference between the carbon−oxygen distances is divided by the carbon−carbon distance.

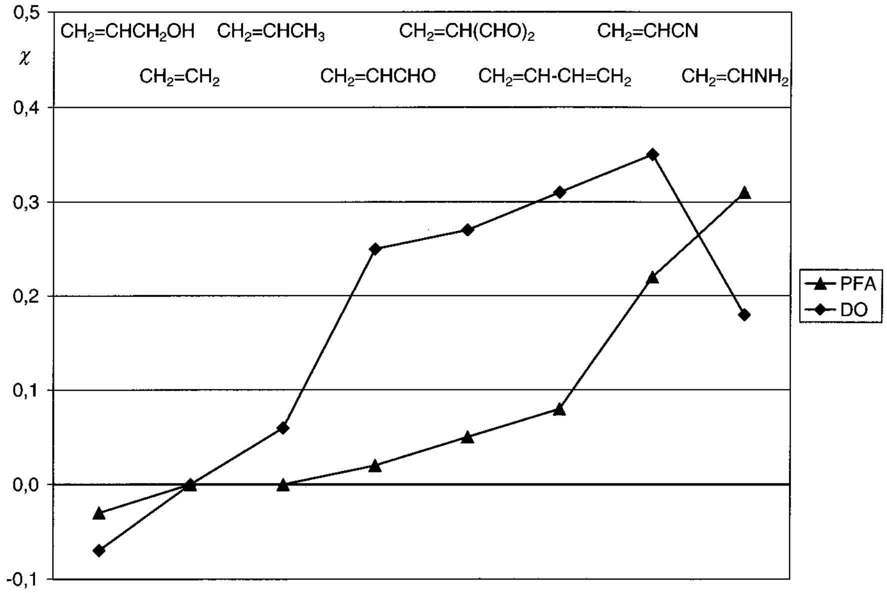

Figure 2. The extent of asymmetry χ in the TSs for olefin epoxidation with PFA and DO.

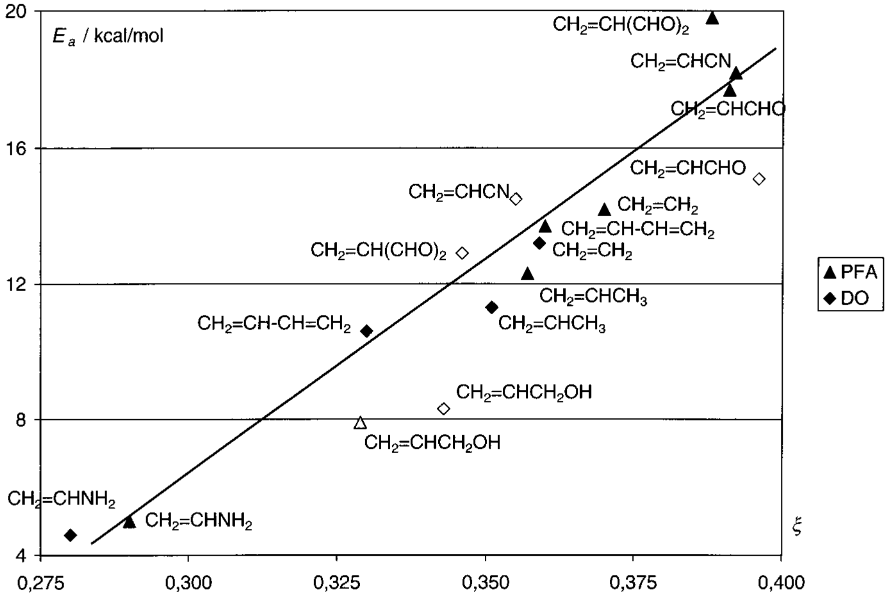

Figure 3. Relation between the activation energies E_a and the extent of reaction ξ. Gray: epoxidation of allylic alcohol; white: epoxidation of electron-poor olefins by dioxirane.

The reactions with most of the other substrates have asymmetric transition structures with positive χ values (Table 1), indicating that the bond to the terminal carbon atom C1 is formed first. The TS for the epoxidation of allylic alcohol is the only exception: the χ value is negative, which means that the O1−C2 bond is formed prior to the O1−C1-bond formation.[22] A comparison between the TSs for PFA and DO is given in Figure 2. It is interesting that the epoxidations of most of the substrates with dioxirane are much more asynchronous than the reactions with peroxyformic acid as oxidant.

The calculated activation energies E_a and reaction energies E_r are also listed in Table 1. The epoxidation of olefins with PFA is highly exothermic by 40−50 kcal/mol; in each case, the reaction with DO is more exothermic by 5.6 kcal/mol. A prediction of reactivity and TS geometries based on thermochemical data would be very useful, but both the Bell−Evans−Polanyi principle[23] and the Hammond postulate[24] fail: there is neither a relation of the reaction energies to the activation barriers nor to the extent of reaction (Table 1). Instead, we find a remarkable correlation between the extent of reaction ξ at the TS and the activation energies E_a. The earlier the transition state on the reaction coordinate, the lower is the activation barrier, as demonstrated in Figure 3. The activation energies for the epoxidations with PFA are increased by electron-withdrawing groups and decreased

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[22] The TS geometries for the epoxidation of butadiene and acrylonitrile with PFA optimized by Bach, Glukhovtsev, and co-workers using the QCISD ab initio method show a smaller extent of asymmetry than do the stationary points on the B3LYP potential-energy surface (ref 1i).

[23] (a) Bell, R. P. *Proc. R. Soc. London, Ser. A* **1936**, *154*, 414. (b) Evans, M. G.; Polanyi, M. *J. Chem. Soc., Faraday Trans.* **1936**, *32*, 1340.

[24] Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

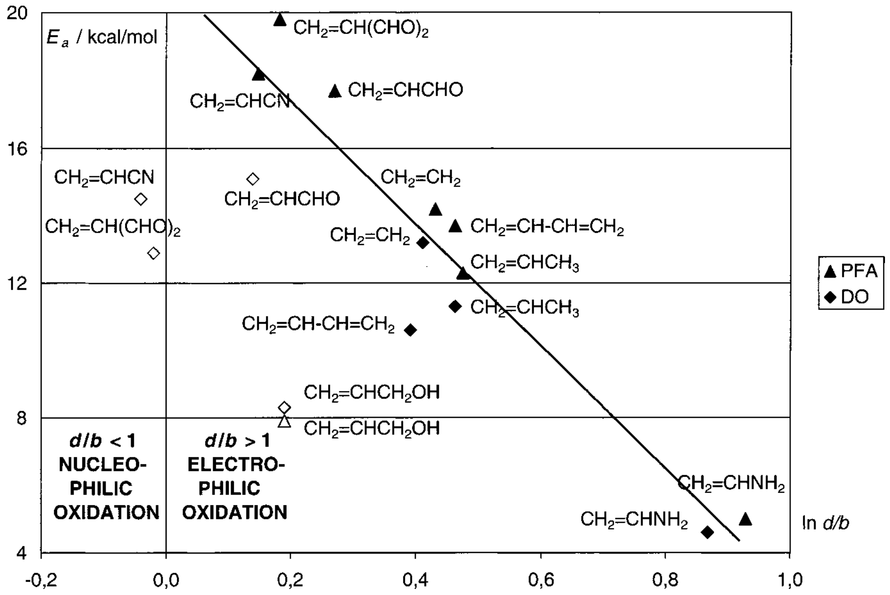

Figure 4. Relation between the activation energies E_a and the CDA parameter ln(*d*/*b*). Gray: epoxidation of allylic alcohol; white: epoxidation of electron-poor olefins by dioxirane.

by electron-donating substituents. For instance, the E_a values are 14.2 kcal/mol for ethylene, 5.0 kcal/mol for vinylamine, and 18.2 kcal/mol for acrylonitrile. The theoretically predicted activation barriers for the epoxidation of most of the substrates by DO are very similar to the PFA results (Table 1, Figure 3). However, there is a considerable difference in the activation barriers for the alkenes with electron-withdrawing groups (white rhombuses in Figure 3). While these substrates are less reactive than ethylene in the reaction with PFA as oxidant, the activation energies for the epoxidation with DO are about the same for ethylene and the alkenes with electron-withdrawing groups. For instance, E_a values of 13.2 kcal/mol for ethylene, 4.6 kcal/mol for vinylamine, and only 14.5 kcal/mol for acrylonitrile have been predicted (Table 1).

Electronic Character and Reactivity. We have studied the electronic character of the transition states using Charge Decomposition Analysis (CDA)[8] as probe. All transition states have been analyzed in terms of donor and acceptor interactions between the fragments olefin and oxidant; the results are given in Table 2. This approximation is justified since the transition states are early and the rest terms Δ, which describe the interactions among the vacant orbitals of both fragments, are close to zero (Table 2). The electrophilicity of the oxidant is considered by charge donation *d* from occupied olefin orbitals into vacant oxidant orbitals in the TS while the nucleophilicity is described by back-donation *b* from occupied oxidant orbitals into vacant olefin orbitals. In the discussion, we focus on the *d*/*b* ratio; the oxidant is electrophilic if $d/b > 1$ while the oxidant is nucleophilic if $d/b < 1$.

The analysis clearly identifies peroxyformic acid as electrophilic oxidant. For all olefins, *d*/*b* values larger than 1 are obtained (Table 2). The *d*/*b* ratio for ethylene epoxidation with PFA is 1.54. Substituents which increase the electron density at the C=C bond lead to larger *d*/*b* values, for example vinylamine (2.53). The TSs for alkenes with electron-withdrawing groups have *d*/*b* ratios smaller than for ethylene, for instance acrylonitrile (1.16). A remarkable relation of the ln(*d*/*b*) values to the activation energies of olefin epoxidation with PFA has been found, as demonstrated in Figure 4.[25] The epoxidation of allylic alcohol is the only exception (grey triangle in Figure 4). The reason for this exception is the stabilization of the TS for the epoxidation of allylic alcohol by a hydrogen bond between the O−H group of the substrate and the O atoms of the oxidant.[26] This hydrogen bond decreases both the electron density at the oxygen atoms of the oxidant in the TS and the *d*/*b* value. Note that the hydrogen bond might be an artifact of the gas-phase study.

Table 2. CDA Results of the Transition States for Olefin Epoxidation with Peroxyformic Acid (PFA) and Dioxirane (DO)[a]

ox.	olefin	*d*	*b*	*d*/*b*	*r*	Δ	E_a
PFA	$CH_2{=}CH_2$	0.216	0.140	1.54	−0.326	−0.004	14.2
DO		0.214	0.141	1.51	−0.362	−0.003	13.2
PFA	$CH_2{=}CH(CH_3)$	0.208	0.129	1.61	−0.309	−0.003	12.3
DO		0.206	0.129	1.59	−0.344	−0.002	11.3
PFA	$CH_2{=}CH(CH{=}CH_2)$	0.201	0.126	1.59	−0.305	−0.002	13.7
DO		0.186	0.125	1.48	−0.314	−0.004	10.6
PFA	$CH_2{=}CH(NH_2)$	0.180	0.071	2.53	−0.219	−0.003	5.0
DO		0.179	0.075	2.38	−0.248	−0.001	4.6
PFA	$CH_2{=}CH(CN)$	0.200	0.171	1.16	−0.369	−0.004	18.2
DO		0.177	0.183	0.96	−0.384	−0.006	14.5
PFA	$CH_2{=}CH(CHO)$	0.211	0.160	1.31	−0.363	−0.001	17.7
DO		0.193	0.167	1.15	−0.378	−0.005	15.1
PFA	$CH_2{=}C(CHO)_2$	0.203	0.169	1.20	−0.372	−0.001	19.8
DO		0.182	0.185	0.98	−0.389	−0.005	12.9
PFA	$CH_2{=}CH(CH_2OH)$	0.233	0.191	1.21	−0.303	−0.007	7.9
DO		0.201	0.165	1.21	−0.353	−0.001	8.3

[a] Donation *d* (olefin→oxidant), back-donation *b* (olefin←oxidant), repulsive polarization *r* (olefin:oxidant), and rest term Δ. Calculated (B3LYP/6-31G(d,p)) activation energies E_a (kcal/mol).

The CDA results of the transition states for the olefin epoxidations with dioxirane are remarkable. For most of

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(25) We have chosen a plot of E_a versus ln(*d*/*b*) instead of *d*/*b* since the definition of the donor and the acceptor is arbitrary.

(26) Most of the recent theoretical studies by Bach and co-workers and Sarzi-Amadè and co-workers focused on the hydrogen-bond directivity in the transition states for the epoxidation of allylic alcohols, see refs 1 and 2. For a recent experimental contribution, see: Adam, W.; Wirth, T. *Acc. Chem. Res.* **1999**, *32*, 703. The allylic-alcohol epoxidation by methyltrioxorhenium(VII) compounds was very recently clarified by Di Valentin et al.: Di Valentin, C.; Gandolfi, R.; Gisdakis, P.; Rösch, N. *J. Am. Chem. Soc.* **2001**, *123*, 2365.

Table 3. Frontier Orbitals of the Reactants,[a] Energies ϵ (in au, at the B3LYP/6-31G(d,p) Level), and Coefficients c (B3LYP/STO-3G//B3LYP/6-31G(d,p)) of the π and π^* Orbital of the C=C Bond which Is Oxidized[b]

		π					π^*				
molecule	sym	orb	Γ	ϵ	$\lvert c(p_z@C1)\rvert$	$\lvert c(p_z@C2)\rvert$	orb	Γ	ϵ	$\lvert c(p_z@C1)\rvert$	$\lvert c(p_z@C2)\rvert$
$CH_2{=}CH_2$	D_{2h}	HOMO	b_{3u}	−0.267	0.63	0.63	LUMO	b_{2g}	0.017	0.81	0.81
$CH_2{=}CH(CH_3)$	C_s	HOMO	a''	−0.250	0.64	0.59	LUMO	a''	0.027	0.79	0.79
$CH_2{=}CH(CH{=}CH_2)$	C_{2h}	HOMO	a_g	−0.229	0.54	0.37	LUMO	a_u	−0.023	0.64	0.44
$CH_2{=}CH(NH_2)$	C_1	HOMO	a	−0.200	0.61	0.33	LUMO	a	0.051	0.76	0.80
$CH_2{=}CH(CN)$	C_s	HOMO	a''	−0.289	0.56	0.48	LUMO	a''	−0.056	0.75	0.57
$CH_2{=}CH(CHO)$	C_s	HOMO-1	a''	−0.293	0.59	0.53	LUMO	a''	−0.065	0.64	0.40
$CH_2{=}C(CHO)_2$	C_s	HOMO-2	a''	−0.306	0.58	0.49	LUMO	a''	−0.098	0.68	0.37
$CH_2{=}CH(CH_2OH)$	C_1	HOMO-1	a	−0.277	0.60	0.56	LUMO	a	0.019	0.78	0.78

[a] PFA (C_s): HOMO (a'') −0.295, LUMO+1 (a') −0.023. DO (C_{2v}): HOMO (a_2) −0.275, LUMO (b_2) −0.031. [b] The terminal carbon atom is denoted C1.

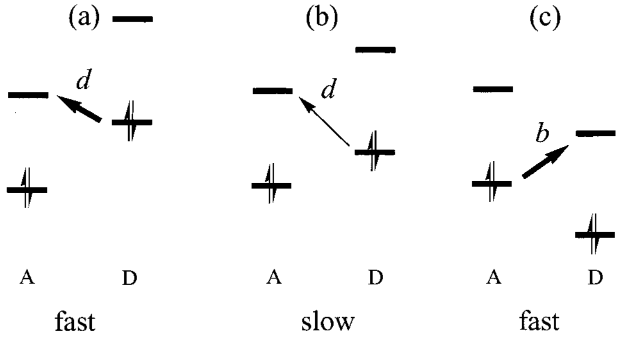

Figure 5. Predominant orbital interactions as the origin of reactivity.

the substrates, *d*/*b* values very similar to the epoxidation with PFA have been obtained. However, alkenes with electron-withdrawing groups have *d*/*b* values < 1, indicating that they are attacked by dioxirane in a nucleophilic rather than electrophilic way. For instance, a *d*/*b* value of 0.96 has been found with acrylonitrile as substrate. The epoxidation of alkenes with electron-withdrawing substituents by DO (white rhombuses in Figure 4) is significantly faster than the corresponding reactions with PFA, in contrast to the epoxidation of the other alkenes. One may compare the oxygen-transfer reactions with simple cycloadditions[27,28] such as Diels–Alder reactions: One reactant is denoted *donor* D, the other reactant is denoted *acceptor* A. Assume that the donor is activated by electron-donating substituents, which increase the frontier-orbital levels of D. Then, electron donation *d* from D to the A will provide the predominant interaction and the reaction is expected to be fast (Figure 5a). A decrease of the orbital levels of D relative to A leads to a weaker donation and a smaller reactivity (Figure 5b). However, a further relative decrease of the frontier orbitals of D might reverse the orbital interactions and cause back-donation *b* from A to D to be more important than *d*, which can result in a higher reactivity (Figure 5c). The same argument holds for the epoxidation transition states analyzed in terms of donor–acceptor interactions between the fragments olefin (*donor*) and dioxirane (*acceptor*).

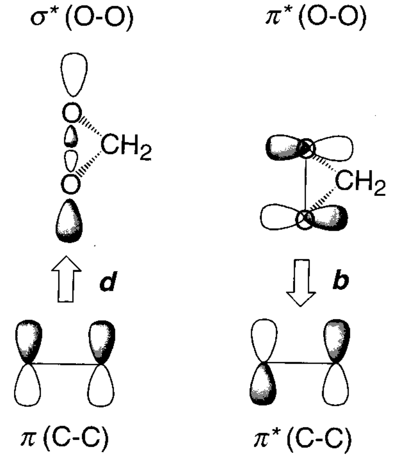

Figure 6. Most important contributions to donation *d* and back-donation *b* in the TS for olefin epoxidation with DO.

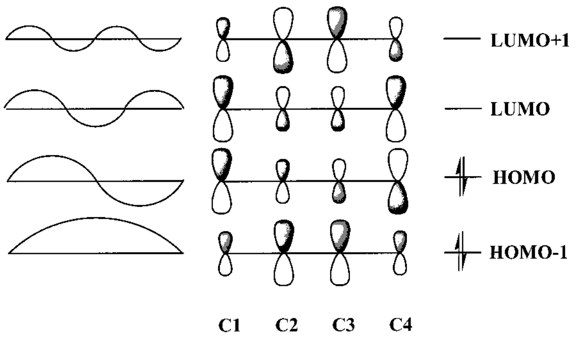

Figure 7. Relation between the eigenfunctions of a particle in a box and the frontier-orbital coefficients of conjugated systems.

The CDA of the transition states gives insight into the orbital interactions which provide the dominant contributions to *d* and *b*. For both oxidants, it has been found that donation mainly proceeds from the π orbital of the olefin into the σ^* orbital of the O–O bond while back-donation *b* is characterized by the interaction between the occupied π^* lone pair of the O–O bond and the vacant π^* orbital of the C=C bond. This is illustrated in Figure 6 for the epoxidation of ethylene with dioxirane. Since donation is the most important orbital interaction in the TS, the asymmetry in the transition states can be explained by the p_z coefficients of the olefin π orbital at the carbon atoms C1 and C2. There is a relation to the eigenfunctions of the simple particle-in-a-box model (Figure 7); the p_z-orbital coefficient at the terminal carbon atom C1 in the HOMO of conjugated systems is larger than at C2 (Table 3). In the epoxidation of conjugated

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(27) (a) Fukui, K. *Theory of Orientation and Stereoselection*; Springer: Berlin, 1970. (b) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976.

(28) (a) Sustmann, R. *Tetrahedron Lett.* **1971**, *29*, 2717. (b) Sustmann, R. *Tetrahedron Lett.* **1971**, *29*, 2721. (c) Houk, K. N. *J. Am. Chem. Soc.* **1973**, *95*, 4092. (d) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361. (e) Sauer, J.; Schubert, R. *Angew. Chem., Int. Ed.* **1980**, *19*, 779. (f) Nelson, D. W.; Gypser, A.; Ho, P. T.; Kolb, H. C.; Kondo, T.; Kwong, H.-L.; McGrath, D. V.; Rubin, A. E.; Norrby, P.-O.; Gable, K. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 1840. (g) Gothelf, K. V.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 863.

olefins, the bond between the oxidant and the terminal carbon atom is therefore formed first. Although the coefficient at the terminal carbon atom C1 of allylic alcohol is also larger than at C2, the bond to C2 is formed before the other C−O bond due to the presence of the hydrogen bridge.

It is interesting to note that the difference in the nature of PFA and DO in their reactions with electron-poor alkenes cannot easily be predicted, if at all, by properties of the free oxidants. The frontier-orbital energies of DO are only slightly higher than the corresponding levels of PFA (Table 3). The lone pairs at the transferred oxygen of DO have a higher s character than those of PFA which becomes evident from an NBO analysis[29] and from the fact that the valence angle at the O1 oxygen in the latter oxidant is larger. The biphilic character of dioxirane is clearly reflected by the transition states for the epoxidation of alkenes bearing electron-withdrawing groups: The extent of reaction is smaller, the extent of asymmetry is larger, and the activation barriers are lower than for the corresponding transition states of peroxyformic acid.

Conclusions

(i) Former experimental studies suggested that both peroxy acids and dioxiranes are electrophilic oxidants: thianthrene 5-oxide is preferentially oxidized at its sulfide moiety and negative ρ values of Hammett studies on the epoxidation of substituted styrenes were reported.

(ii) Charge Decomposition Analysis (CDA) has been employed for a quantum-chemical probe for the electronic character of oxygen-transfer reactions. The analysis of the transition states for the epoxidation of 8 substituted olefins has revealed that peroxyformic acid (PFA) is an electrophilic oxidant. A correlation between the electronic character and reactivity has been found: the more electrophilic the attack on the C=C bond is, the faster the olefin epoxidation with PFA. There is also a significant relation between the activation energies and the extent of reaction; the faster reactions have earlier TSs.

(iii) In contrast, dioxirane (DO) has been identified as both electrophilic and nucleophilic oxidant for olefins, depending on the substituents at the C=C bond. Alkenes with electron-withdrawing groups are attacked by DO in a nucleophilic way. The biphilic nature of dioxirane is not evident from properties of the free oxidant. The transition states for the epoxidation of electron-poor olefins with dioxirane are characterized by a small extent of reaction, a large extent of asymmetry, and a comparably low activation barrier.

(iv) Solvation effects and substituents at the oxidants will also influence the electronic character of oxygen transfer. For instance, dimethyldioxirane is less electrophilic or more nucleophilic than DO while methyl(trifluoromethyl)dioxirane is more electrophilic.

(v) The results of this study will encourage experimentalists to perform additional investigations of the electronic character of oxygen-transfer reactions. One Referee suggested Hammett studies on the epoxidation of highly electron-deficient test substrates such as cinnamates, benzylidene malonic acid derivatives, and beta-nitro styrenes.

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[29] Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.