On the electronic character of oxygen-transfer reactions†

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Charge Decomposition Analysis (CDA) applied to transition states of ethylene epoxidation is a quantum-chemical probe for the electronic character of oxygen-transfer reactions.

The insight into the electronic character of oxygen-transfer reactions, *i.e.* whether the oxidant attacks the substrate in an electrophilic or nucleophilic way, is used as a tool for an efficient development of catalysts for these reactions.[1] The most popular probe is the chemoselective oxidation of thianthrene 5-oxide introduced by Adam and co-workers.[2] Information about the electronic character of the transition states of olefin epoxidation is also provided by the effect of alkyl[3] and aryl[4] substituents at the C=C double bond on reactivity. A quantum-chemical probe has not been suggested yet, which is somewhat astonishing because the geometry optimization of transition states and the analysis of their electronic structure are key applications of modern computational chemistry. Hence, the principal aim of this work was to find a quantum-chemical probe for the electronic character of oxygen-transfer reactions.

In experimental work and recent theoretical studies by Bach *et al*., Houk *et al*. and others, it was shown that olefin epoxidation with organic peracids[5] and dioxiranes[6] follows a concerted oxygen-transfer mechanism with a *spiro* oxygen atom in the transition state (TS). The topology of the TS is coarctate.[7] Very recently, Rösch *et al.*[8,9] and we[10] supported an analogous mechanism for ethylene epoxidation by Herrmann-type complexes $[ReO(O_2)_2(CH_3)]$[8] and Mimoun-type complexes $[MoO(O_2)_2(OPR_3)]$,[9,10] as postulated by Sharpless *et al.*[11] For this work, we re-optimized TSs for ethylene epoxidation using standard density functional (DFT) methods for oxidations.[12] Calculated TS structures for dimethyldioxirane (DMDO), MCPBA, and $[ReO(O_2)_2(CH_3)]$ as oxidants are shown in the ESI†; selected geometrical parameters are given in Table 1.

The most simple tool for electronic-structure analysis is the calculation of atomic partial charges. The sum of NPA charges[13] at ethylene in the TSs are listed in Table 1. The values for all reactants indicate that, at the TSs, electronic charge has migrated from ethylene to the oxidant. In order to gain additional insight into the nature of the electronic interactions in the TSs, we utilized Charge Decomposition Analysis (CDA).[14,15] The Kohn-Sham MOs of a TS are expressed as a linear combination of the MOs of the fragments ethylene ('donor') and oxidant ('acceptor') in the geometry of the TS. 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.[14] For the electronic character of oxygen-transfer reactions, the ratio $d:b$ in the TS is important. Oxidants with $d:b > 1$ are electrophilic, those with $d:b < 1$ are nucleophilic. Table 2 shows the CDA results. The most important fragment-orbital interactions in the TS of the ethylene epoxidation with $[ReO(O_2)_2(CH_3)]$ are visualized in Fig. 1. We draw the following conclusions:

(i) Small rest terms ($\Delta \approx 0$, Table 2) indicate that the electronic structure of the epoxidation transition states can be properly described in terms of donor–acceptor interactions between the fragments, ethylene and oxidant. This was to be expected from the Hammond postulate[16] because the strongly exothermic reactions have early TSs.

(ii) For all oxidants, donation, d, is an interaction between the ethylene HOMO and the σ^* orbital of the O–O bond.[17] Note that the σ^* orbital of the O–O bond does not neccessarily correspond to the LUMO of the free oxidant. The interaction between the lone pairs at the transferred oxygen atom and the ethylene LUMO provides the predominant contribution to backdonation, b, Fig. 1.

(iii) For all epoxidations investigated here, donation from ethylene to the oxidant is more important than back-donation, indicating an electrophilic attack of the oxidant on the olefin. The reason is that donation occurs earlier on the reaction coordinate. The O–O σ^* orbital of the oxidant has a high coefficient from the p orbital pointing directly toward the

Table 1 Analysis of the transition states of ethylene epoxidation. C–O and C–C distances a [Å], sum q [e] of the NPA charges of the CH_2 moieties of the ethylene fragment, ratio $d:b$ of donation d and back-donation b in CDA, and activation energies E_a (B3LYP/III+//B3LYP/II)[a] [kcal mol^{-1}]. ZPE-corrected values (B3LYP/II)[a] in parentheses

	a			q			
Oxidant	C1–O	C2–O	C1–C2[b]	$C1H_2$	$C2H_2$	$d:b$	E_a
Dimethyldioxirane (DMDO)	1.977	1.977	1.373	0.199	0.199	1.32	17.1 (17.9)
Dioxirane (DO)	2.011	2.011	1.370	0.190	0.190	1.50	12.0 (12.8)
HCO_3H	2.029	2.029	1.369	0.190	0.190	1.55	14.6 (15.2)
m-Chloroperbenzoic acid (MCPBA)	2.037	2.037	1.368	0.185	0.185	1.56	15.4 (16.0)
$[MoO(O_2)_2(OP(CH_3)_3)]$ ($[Mo]O_2$)	2.078	2.186	1.360	0.160	0.129	1.76	16.6 (17.5)
$[ReO(O_2)_2(CH_3)]$ ($[Re]O_2$)	2.051	2.164	1.363	0.191	0.164	2.07	13.7 (14.5)

[a] For computational details, see ESI or: D. V. Deubel and G. Frenking, *J. Am. Chem. Soc.*, 1999, **121**, 2021. [b] Free ethylene: 1.331 Å.

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† Electronic supplementary information (ESI) available. Geometries optimized at the B3LYP/II level of the transition states for ethylene epoxidation with DMDO, MCPBA, and $[ReO(O_2)_2(CH_3)]$ and predominant orbital interactions of donation d and backdonation b according to the CDA of the transition states for DMDO and MCPBA. See http://www.rsc.org/suppdata/cc/b0/b006280o/

Table 2 CDA results of the transition states. Donation d ($C_2H_4 \longrightarrow$oxidant), back-donation b ($C_2H_4 \longleftarrow$ oxidant), repulsive polarization r ($C_2H_4 \longleftrightarrow$oxidant), and rest term Δ

Oxidant	d	b	$d{:}b$	r	Δ
DMDO	0.231	0.175	1.32	−0.393	−0.003
DO	0.223	0.149	1.50	−0.353	−0.003
HCO_3H	0.229	0.148	1.55	−0.326	−0.004
MCPBA	0.227	0.146	1.56	−0.319	−0.004
$[Mo]O_2$	0.237	0.135	1.76	−0.312	−0.004
$[Re]O_2$	0.230	0.111	2.07	−0.276	−0.005

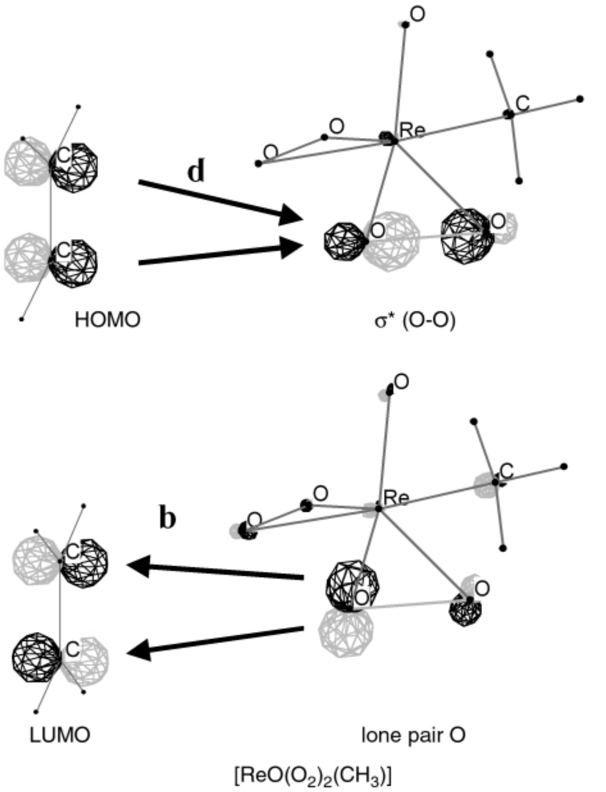

Fig. 1 Predominant orbital interactions of donation d and backdonation b according to CDA of the transition state for ethylene epoxidation with $[ReO(O_2)_2(CH_3)]$.

ethylene. Thus, at the long C(ethylene)–O distances of about 2.0 Å in the TS, the overlap integral is larger for donation than for back donation. While donation is approximately equal for all investigated epoxidations, the b values vary signficantly with the C–O distances (Table 2).

(iv) Due to $d{:}b > 1$, an increase of the olefin HOMO energy originated by alkyl substituents will accelerate epoxidation if steric effects are negligible. This is experimentally[3] and theoretically[5c,5g] confirmed. Negative ρ values from Hammett studies indicate a decrease of electron density at the C=C bond in the TS.[4]

(v) The ratio $d{:}b$ is a quantum-chemical probe for the electronic character of oxygen-transfer reactions. The larger the value of $d{:}b$, the more electrophilic is the oxidant. Electrophilicity increases in the series DMDO < DO < HCO_3H = MCPBA < $[Mo]O_2$ < $[Re]O_2$. The metal peroxides are the most electrophilic oxidants.

(vi) The attempt to quantitatively correlate our electrophilicity scale with experimental parameters fails due to their dependence on reaction conditions,[2,4] such as temperature and solvent, and because of the lack of accessible data.

(vii) A relation between *electronic character* (*i.e.* $d{:}b$) and *reactivity* (*i.e.* activation energy E_a) is only found within the same class of oxidants, *e.g.* for the two dioxiranes.

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