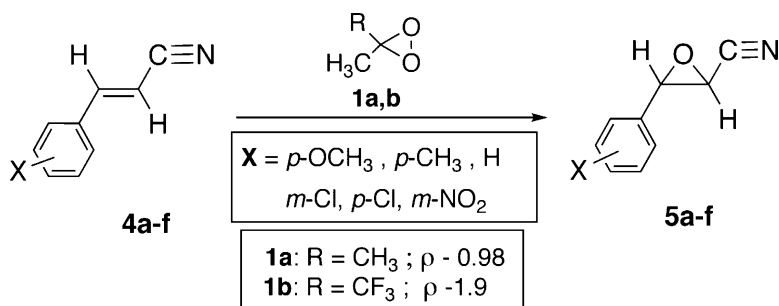


Concerning the Reactivity of Dioxiranes. Observations from Experiments and Theory

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Concerning the Reactivity of Dioxiranes. Observations from Experiments and Theory

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Abstract: The challenging hypothesis of a “biphilic” (i.e., electrophilic vs nucleophilic) character for dioxirane reactivity, which envisages that electron-poor alkenes are attacked by dioxiranes in a nucleophilic fashion, could not be sustained experimentally. Rate data, which estimate Hammett “rho” values for the epoxidation of 3- or 4-substituted cinnamitriles X-Ph-CH=CH-CN, unequivocally allow one to establish that dioxiranes epoxidize *electrophilically* even alkenes carrying electron-withdrawing groups. The greater propensity of methyl(trifluoromethyl)dioxirane TFDO (**1b**) to act as an electrophilic oxidant with respect to dimethyldioxirane DDO (**1a**) parallels the cathode reduction potentials for the two dioxiranes, as measured by cyclic voltammetry. A simple FMO approach for alkene epoxidation is helpful to conceive a likely rationale for the greater oxidizing power of TFDO as compared to DDO.

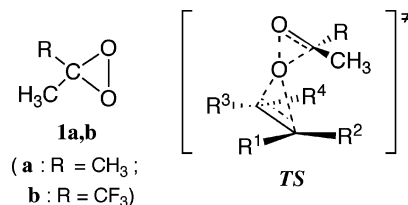
Introduction

In the past several years dioxiranes have rapidly grown into one of the more useful oxidation processes in the arsenal of synthetic chemists.¹ Their unique reactivity ranges from the transfer of an oxygen atom to “unactivated” C–H bonds of saturated hydrocarbons, to epoxidations, to the oxidation of heteroatoms containing a lone pair of electrons such as amines and sulfides. In fact, applications in synthesis of the currently popular dimethyldioxirane (**1a**) (DDO)^{2a} and of methyl(trifluoromethyl)dioxirane (**1b**) (TFDO)³ in isolated form have proliferated the access to key products that are useful in organic synthesis.^{1–5}

The efficient oxyfunctionalization of unactivated C–H bonds of alkanes under extremely mild conditions undoubtedly ranks

at present as the highlight of dioxirane chemistry.¹ For this remarkable transformation, the high stereoselectivity as well as kinetic evidence all point to an oxenoid (electrophilic) mechanism of insertion.¹

Given the value of epoxides as synthons, among the myriad of useful dioxirane oxidations, the most common reaction undoubtedly remains the oxidation of carbon–carbon double bonds of alkenes.^{1–5} In fact, the use of dioxiranes today rivals that of peracids in epoxidation reactions because of the enhanced rates of reaction and of their performance under neutral conditions, providing access to even highly sensitive epoxides. Alkenes of various kinds, either electron-rich or electron-poor, have been successfully epoxidized employing dioxiranes.⁵



Much of the early^{4a} and subsequent experimental evidence, including the *syn*-stereospecific course of dioxirane epoxidations and the greater reactivity of *cis* alkenes with respect to their *trans* isomers,⁴ kinetics, and H/D isotope effects all have pointed to a substantially concerted mechanism,⁴ akin to that of epoxidation by peracids.^{6,7} A *spiro* transition state (**TS**) for the

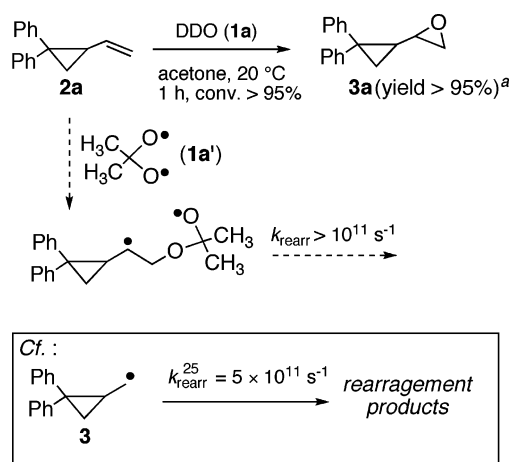
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Chart 1^a

^a No products derived from rearrangement were detected (ref 11).

dioxirane approach to the double bond was suggested to be consistent with all these data.^{4b,d} Following the pioneering theoretical work by Bach,⁷ numerous computations also substantiated the claim of a largely concerted mechanism. The most recent calculations at a high-level of theory on this topic confirm the previous notion envisaging a concerted nucleophilic attack by the alkene π bond at the O–O bond of the dioxirane electrophile along an S_N2 -type coordinate, much in the fashion of the mechanism well established for nucleophilic attack of common peroxides.⁸ Calculations have shown that uneven substitution of the C=C can cause the transition state to become unsymmetrical, but no intermediates were located on the potential surface.⁷

Because of their relevance in synthesis, mechanistic studies of key transformations involving dioxiranes have continued unabated during the past decade.¹ In this regard, the involvement of radical pathways⁹ could be discounted also for dioxirane epoxidations on the basis of considerable evidence derived from careful experiments and computations.^{4e,10}

Furthermore, the application of the ultrafast (2,2-diphenyl)cyclopropylcarbinyl radical (**3**) probe^{11a} to the transformation of 1,1-diphenyl-2-vinylcyclopropane (**2a**) into the corresponding epoxide (**3a**), yielding no rearrangement products (Chart 1), allowed us to rule out pathways involving discreet radical intermediates.^{11b}

Concerning the electronic character of the dioxirane oxygen transfer from dioxiranes to alkenes, a more appealing mechanistic question has been advanced recently by Deubel and co-workers.¹² In fact, using high-level computational methods, these authors employed Charge Decomposition Analysis (CDA) to estimate the donor–acceptor interactions in the transition

Table 1. Relative Rates of Epoxidation of Cinnamitriles with Dioxiranes **1a,b** in Acetone Solvent

entry	substrate	substituent	rel. rate ($k^{\text{rel}}/k^{\text{ref}}$) ^a		$10^3 k_2$ ($\text{M}^{-1} \text{ s}^{-1}$)	
			DDO (1a) ^b	TFDO (1b) ^c	DDO (1a)	TFDO (1b)
1	(<i>E</i>)- 4a	<i>p</i> -OCH ₃	7.02			
2	(<i>E</i>)- 4b	<i>p</i> -CH ₃	2.21	4.90		
3	(<i>Z</i>)- 4b'	<i>p</i> -CH ₃	2.19			
4	(<i>E</i>)- 4c	H	1.00	1.00	0.7 ^d	37 ^e
5	(<i>Z</i>)- 4c'	H	1.10	1.95		
6	(<i>E</i>)- 4d	<i>p</i> -Cl	0.84	0.53		
7	(<i>E</i>)- 4e	<i>m</i> -Cl	0.42	0.24		
8	(<i>E</i>)- 4f	<i>m</i> -NO ₂	0.28	0.045		

^a Relative rate coefficients estimated as averages (± 2 –8%) from $\log([A]_0)/\log([B]_0)$; the concentrations of two given competing substrates (A and B) were determined (HPLC) at various times (usually over the first 15–50% of reaction). ^bAt 25.0 °C, with $[\text{DDO}]_0 = 0.05$ –0.08 M and $[\text{Substrate}]_0 = (0.1$ –0.5) $\times 10^{-2}$ M. ^cAt 5.0 °C, with $[\text{TFDO}]_0 = 0.13$ –0.17 M and $[\text{Substrate}]_0 = (0.2$ –0.6) $\times 10^{-2}$ M. ^dAt 25.0 °C, absolute rate constant k_2 , estimated (± 4 –8%) as $(k_1/[\text{E-4c}]_0)$ from runs under pseudo first-order conditions, with $[\text{DDO}]_0 = (0.05$ –0.08) $\times 10^{-2}$ M and $[\text{E-4c}]_0 = (4.0$ –6.5) $\times 10^{-2}$ M. ^eAt 5.0 °C, absolute rate constant k_2 (± 5 –10%) from kinetics run under second-order conditions, with $[\text{TFDO}]_0$ and $[\text{E-4c}]_0$ initial concentrations both ranging (1.5–5.0) $\times 10^{-2}$ M.

structure for the dioxirane epoxidation of alkenes substituted by electron-donor (ED) or electron-withdrawing (EW) substituents. Their conclusion was that the electronic character (electrophilic vs nucleophilic) of the dioxirane depends upon the substituents on the C=C bond of the alkene. For the model alkenes examined, EW substituents on the C=C bond (–CN and –CH=O) designate the dioxirane to behave as a *nucleophilic* oxygen-transfer agent. Deubel cautioned that this peculiar feature of dioxirane reactivity does not derive from the inherent electronic properties of the dioxirane itself, but it becomes manifest from the computed parameters of the transition structures for the dioxirane/alkene pair.¹²

In our view, the interesting hypothesis of a possible electrophilic/nucleophilic dichotomy for dioxirane reactivity, a novel feature not recognized previously, demanded rigorous scrutiny. Therefore, we set out to revisit the transformation above, starting with determining the rates of dioxirane oxidation of a few substituted cinnamitriles aimed at establishing a Hammett LFER. Obviously, this simple approach would allow one to assess *experimentally* the electronic character of the oxidant in the transformation at hand. Along with other pertinent observations concerning dioxirane reactivity, our results are reported below.

Results and Discussion

Using both DDO and TFDO, we have examined the oxidation of cinnamitrile and of a few substituted cinnamitriles (3-, or 4-)X-Ph–CH=CH–CN carrying either EW or ED substituents X on the phenyl moiety (Table 1). Prior to determining the reaction rates, it was verified that at the given conditions the compounds considered are cleanly transformed into their corresponding epoxides in a stereospecific manner, with high yield (>95%) and practically complete conversion, with the

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notable exception of the TFDO oxidation of *E* or *Z* cinnamitriles carrying the $-\text{OCH}_3$ substituted phenyl moiety. In fact, limited to this case, the oxidative scission of the electron-rich aryl moiety by the powerful TFDO was found to prevail. This finding is in agreement with our early reports concerning the TFDO oxidation of catechols and of benzene itself to muconic acids,^{13a} as well as with more recent literature data.^{13b} In most cases, it was found that substrate epoxidation is quite fast, especially when the powerful TFDO is the oxidant. Therefore, we found it appropriate to determine the relative rates by kinetics runs wherein the concentration decay of two substrates competing for excess dioxirane was determined at various times using HPLC. In consideration of the fast rates and of the volatility of TFDO, kinetic runs using this oxidant were conveniently carried out at subambient temperature (5 °C).

Relative rates data are presented in Table 1. For unsubstituted cinnamitrile *E*-**4c**, the absolute epoxidation rate constants with DDO and TFDO were also determined (footnotes *d* and *e*, Table 1). Data in Table 1 show that, with both DDO and TFDO, EW groups in the substrate decrease the rate of epoxidation, whereas the opposite is true with ED substituents. For the DDO runs, a Hammett plot of $\log(k^X/k^H)$ vs σ^+ for the *E*-alkenes (entries 1, 2, 4, 6, 7, and 8) provides an ρ^+ value of -0.98 (r 0.991). A similar plot of relative rates for the TFDO reactions yields $\rho^+ = -1.9$ (r 0.991). Although just a few substituted cinnamitriles were examined, these markedly negative ρ^+ values point to a TS wherein a partial positive charge is developing on the alkene, leaving no doubt that the dioxiranes act as the *electrophile* in these epoxidations.

Kinetic studies by Baumstark and Vasquez allowed these authors to estimate a Hammett ρ^+ of -0.90 for the dioxirane epoxidation of substituted styrenes; the greater reactivity of *Z*-alkenes in the DDO epoxidation of *E/Z* pairs of alkenes was ascribed to steric interactions developing in the TS.^{14a} Also, Murray reported the relative epoxidation rates of a series of 4-substituted (*E*)-ethylcinnamates by DDO, yielding a Hammett $\rho = -1.53$.^{14b}

Data in Table 1 suggest that steric effects are relatively unimportant here, since it is found that the *cis* alkenes are only just a trifle more reactive than their *trans* isomers (cf., entries 2–5). Worthy of note is the finding that the measured absolute rates (Table 1, footnotes *d* and *e*) show that TFDO is over 50 times more reactive than DDO in carrying out the transformation at hand. And this, despite the fact that epoxidations with TFDO were conveniently run at a 5 °C, i.e., well below those using DDO (25 °C). Clearly, TFDO should be the reagent of choice to perform the epoxidation of electron-poor alkenes efficiently. Thus, the reactivity trend TFDO > DDO as electrophilic oxidant is confirmed in the case at hand also. Actually, we found that in the case of substrates more reluctant to undergo dioxirane O-transfer, such as either simple or structurally complex hydrocarbons, TFDO is more reactive than DDO by a factor of almost 10^3 .^{1,4d}

Yet another experimental hint of the more powerful oxidizing power of TFDO with respect to DDO came from the measure of their electrode potential measurement E_p^{cat} by cyclic volta-

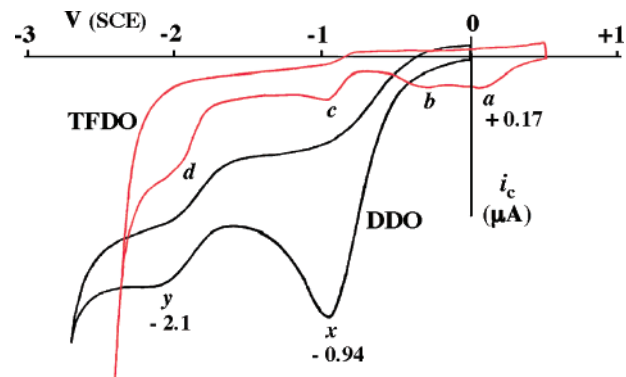


Figure 1. Cyclic voltammetry of DDO **1a** and of TFDO **1b** (red trace), both ca. 2×10^{-3} M in MeCN, at 20 °C. TBAPF₆ (0.1 mol L⁻¹) supporting electrolyte, glassy carbon working electrode, platinum wire counter electrode, SCE reference electrode, 200 mV s⁻¹ scan rate. Wave peaks *a* and *x* are taken to correspond to the one-electron reduction potentials (E_p^{cat}) of TFDO and of DDO, respectively.

metry (CV). Among the readily available electrochemical methods, cyclic voltammetry (CV) techniques are the simplest and the most convenient to use in organic solvents, offering direct access to reduction potentials.^{15,16} Typically, the cyclic voltammograms of most peroxide compounds exhibit irreversible behavior at sweep rates up to 200 mV s⁻¹ and more. This results in the absence of the anodic component on the return potential sweep, largely owing to competition from fast follow-up reactions of the metastable peroxide anion radicals.¹⁶

We ran the CVs of DDO and of TFDO in acetonitrile solvent with 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄N⁺PF₆⁻, TBAP) as supporting electrolyte. In Figure 1 typical CV traces are shown, which were recorded at the conditions given in the footnote.

Carefully purged (Ar gas) DDO solutions gave two irreversible waves with peaks *x* and *y* located at -0.94 and at -2.1 V, respectively (Figure 1). Control experiments allowed us to rule out that any of these waves are due to the O₂/O₂^{•-} couple, residual acetone (also the reduction product of DDO), or impurities. As found for other peroxides,¹⁶ it is likely that the initial electron transfer to give rise to the radical-anion [(CH₃)₂CO₂]^{•-} is accompanied by the scission of the weak O–O bond, forming a ring-opened radical-anion species such as $\bullet\text{O}-\text{C}(\text{CH}_3)_2-\text{O}^-$; from the latter, the rapid formation of a second reducible species should account for the wave with peak *y*. The CV of TFDO presented a more complex case. Ketone-free TFDO was employed in these experiments.^{3d} However, oxygen could not be completely removed by bubbling inert gas through the solutions, since the procedure also depletes substantially this highly volatile dioxirane species.³ Thus, interference by the O₂/O₂^{•-} couple cannot be avoided. As a result, the electrode reduction of TFDO does not result in a “clean” process. It is apparent that, ensuing the initial reduction to the radical anion (peak *a*, +0.17 V), hence to $\bullet\text{O}-\text{C}(\text{CH}_3)(\text{CF}_3)-\text{O}^-$,¹⁷ a rapid consecutive chemical reaction yields yet another metastable

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Table 2. Cathodic Reduction Peak Potentials of Some Organic Peroxides from Cyclic Voltammetry^a

entry	peroxide	E_p^{cat} (V/SCE)	reference
1	TFDO (1b)	+0.17	this work
2	DDO (1a)	-0.94	this work
3	VO(O ₂)(Pic)(H ₂ O) ₂	-1.26	16d
4	WO(O ₂) ₂ (HMPT)	-1.30	16d
5	MoO(O ₂) ₂ (HMPT)	-1.44	16d
6	CH ₃ C(=O)O-OBu- <i>t</i>	-1.49	16a
7	<i>t</i> -BuO-OBu- <i>t</i>	-2.70	16a

^a In acetonitrile solvent with TBAPF₆ (0.1 M) supporting electrolyte (entry 1 and 2), in DMF with 0.1 M TBABF₄ supporting electrolyte for the other peroxide species (entry 3 to 7); see also text and caption of Figure 1.

electroactive species (peak **b**, ca. -0.28 V), which is in turn rapidly consumed. The third shallow wave with its maximum at ca. -0.9 V (peak **c**) appears in a region that is characteristic of the O₂/O₂^{•-} couple in acetonitrile or DMF;^{15,18} the absence of a reversible wave suggests that O₂^{•-} (similarly to other radicals)¹⁹ contributes to the overall chemical process of dioxirane decomposition and it is quickly consumed.¹⁷ In fact, we previously reported evidence concerning a rapid electron-transfer chain reaction mediated by the superoxide ion for TFDO decomposition.¹⁷ Finally, peak **d** (at ca. -2.0 V) might be attributed to the reduction of one ending electroactive species derived from dioxirane decomposition (most likely, 1,1,1-trifluoroacetone).¹⁷ In fact, its depth was observed to increase continuously with time at the expense of the others through the repeated scans.

Obviously, elucidation of the detailed reaction mechanism of dioxirane electrode reduction must await further experiments. Nonetheless, it is clear that the cathodic E_p^{cat} data support the electrophilic nature of these oxidants.¹

Baron and co-workers investigated the voltammetry of a variety of classic organic peroxides in DMF under comparable conditions to those adopted for the dioxiranes at hand. For simple dialkylperoxides and peresters, all yield irreversible broad CV waves, and peaks are positioned over a wide potential range, from -2.70 to -0.59 V/SCE for nonaryl substituted compounds.^{16a} Besides, Bonchio et al. have reported the reduction potentials of several "side-on" peroxy complexes of *d*⁰ transition metals in DMF, again determined by CV under conditions very similar to those mentioned above.^{16d} A few representative cathodic E_p^{cat} values of the latter and those of dialkyl peroxides of choice are listed in Table 2, in comparison to the analogous values determined for dioxiranes.

Inspection of Table 2 indicates that the dioxiranes rank among the most easily reducible peroxides. The E_p^{cat} value recorded for DDO (entry 2) is markedly less negative even than that for the molybdenum side-on peroxometal complex (entry 5), deemed to be the ultimate electrophilic epoxidation reagent.^{12c} It is worthy of note that the reduction potential estimated for TFDO is astoundingly more positive even with respect to DDO by over 1 V. The considerable ease with which TFDO undergoes one-electron reduction is also pointed out by calculations involving the conversion of the dioxiranes at hand into the

corresponding radical anions, i.e., R(CH₃) CO₂ (**1a,b**) + e⁻ → [R(CH₃) CO₂]^{•-}. In fact, our computations for this process at the B3LYP/6-311++G(2d,p) level, including a suitable solvent model (see below), gave $\Delta E = -28.9$ and -30.4 kcal mol⁻¹ in acetone and acetonitrile, respectively, for DDO. In contrast, for TFDO the computed values were $\Delta E = -42.6$ kcal mol⁻¹ in acetone and -43.9 kcal mol⁻¹ in acetonitrile. Therefore, it is reasonable to assume that the relatively large change monitored in reduction energetics is reflected, at least in part, by the greater propensity for electrophilic O-transfer to electron-donor substrates manifested by TFDO with respect to DDO and other classical peroxides.

Theoretical studies support the enhanced reactivity of TFDO with respect to DDO. Although the driving force of dioxirane reactivity has customarily been ascribed to a relief of ring strain,¹⁻⁵ the recent reassessment of the strain energy of DDO (SE = 11 kcal mol⁻¹) by Bach et al.²⁰ suggests this should not play a major role. Rather, dioxirane inclination to peroxide O-transfer might just be due to the favorable enthalpy change attending the formation of a strong C=O π -bond in its reduction product, i.e., the parent ketone. Thus, as in the classic case comparing epoxidations with trifluoroperacetic vs peracetic acid,²¹ the increased reactivity of TFDO with respect to DDO has been ascribed largely to the inductive effect exercised by the CF₃ group.⁷

High-level theoretical work on dioxirane epoxidations of representative alkenes has supported the higher reactivity of TFDO. For instance, at the B3LYP/6-31+G(d,p) level of theory the computed activation barriers (ΔE^\ddagger) for the epoxidation of ethene with DDO and with TFDO are 17.7 and 11.1 kcal mol⁻¹, respectively; at the QCISD(T)//QCISD/6-31+G(d,p) level the computed ΔE values were 15.5 kcal mol⁻¹ for DDO and 11.1 kcal mol⁻¹ for TFDO.^{7,21a} However, it is well recognized that in the condensed phase these barriers could be significantly lower.^{7,23}

In Figure 2 we report a summary of our own computations regarding the optimized transition structures of dioxirane epoxidation of ethene and of acrylonitrile both in the gas phase and in acetone solvent. Inspection of Figure 2 shows that replacing one hydrogen atom with the cyano group in ethene makes the transition structures nonsymmetrical, as expected.^{7,22} These data suggest that upon passing from a gas to condensed phase (acetone solvent) the epoxidations rates should benefit by a decrease of activation barriers of some 1.5–2.0 kcal mol⁻¹, except the case of TFDO reaction with acrylonitrile (TS **d**) where there is practically no change in the computed ΔE^\ddagger .

The data also show that the powerful TFDO is a more effective O-transfer agent than DDO in its reaction with both ethene and with acrylonitrile either in the gas phase or in

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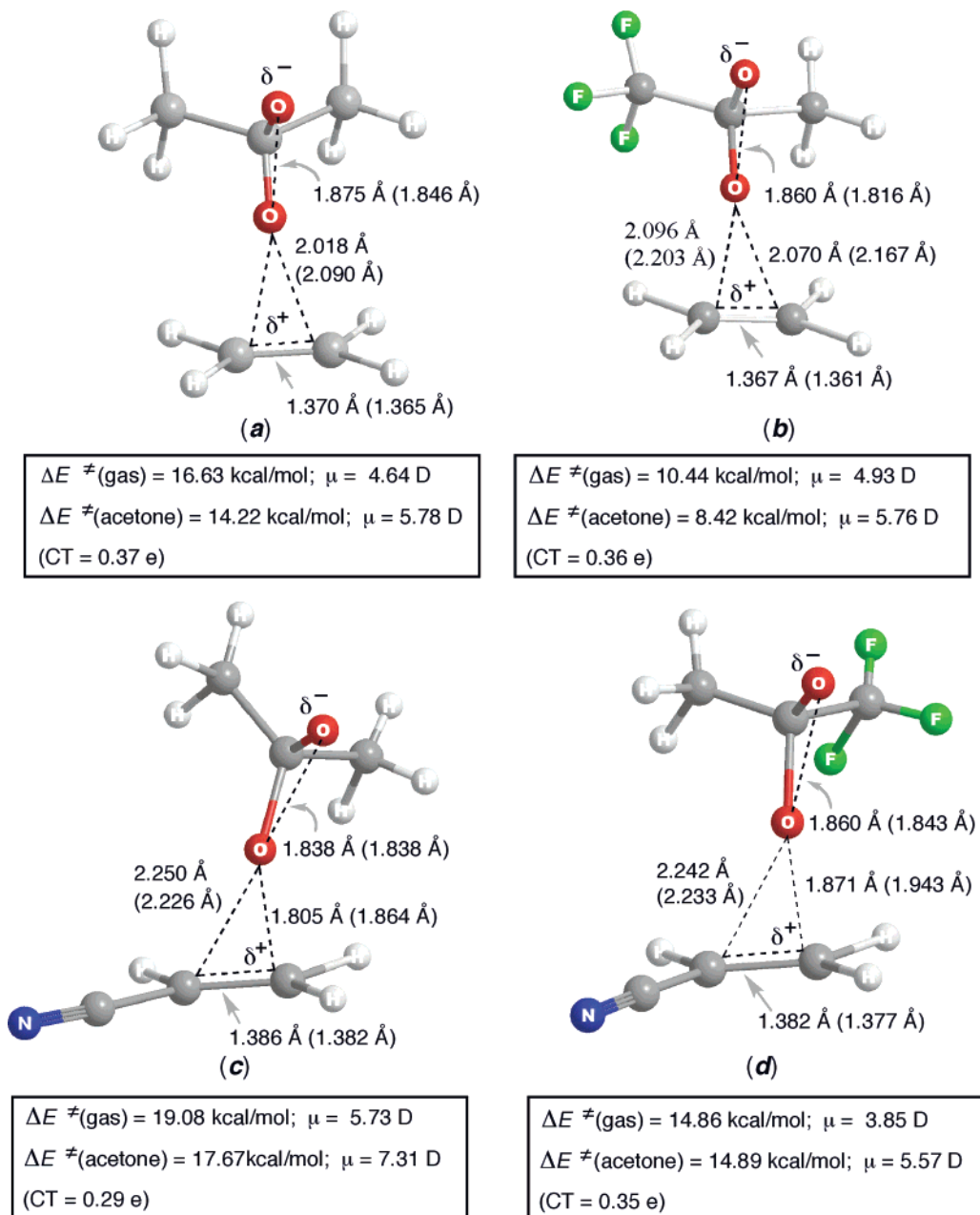


Figure 2. Transition structures for the epoxidation of ethene with DDO (*a*) and by TFDO (*b*), as compared to their analogue TSs for the epoxidation of acrylonitrile, (*c*) and (*d*) respectively. All structures were optimized at the B3LYP/6-31+G(2d,p) level of theory, both in the gas phase and in solvent acetone. Bond lengths for structures in solution are shown in parentheses. The fraction of charge transfer (CT) from alkene to dioxirane in acetone is given in electron units.

acetone; in fact, a $\Delta\Delta E^\ddagger$ of ca. -6 kcal mol^{-1} applies (cf., TS *a* and *b*), whereas the computed activation barriers for the TFDO epoxidation of acrylonitrile are lower than those for DDO by about 4.2 and $2.8 \text{ kcal mol}^{-1}$ in the gas phase and acetone, respectively (cf., TS *c* and *d*). Notice that a difference of $2.8 \text{ kcal mol}^{-1}$ in E_a would make TFDO epoxidations of acrylonitrile in solvent acetone to occur faster than those with DDO by a factor of over 10^2 at 25°C . More important, the charge-transfer (CT) figures computed for all transition structures leave no doubt that the electron donation is from the alkene to the dioxirane. This is in complete agreement with the vast majority of theoretical and experimental literature reports.⁷

While long-lived radical intermediates could be ruled out on the basis of both theoretical and experimental data, it should be mentioned that, consistent with previously reported theoretical

work,^{7,21d,e} there is a certain amount of diradicaloid character in the TS for DDO alkene epoxidation.

We believe that, in addition to precise computations of transition state energies, an analysis of FMO interactions also corroborates the higher reactivity found for TFDO. In Table 3 we report the energy levels for the significant MO of DDO and of TFDO calculated at various levels of theory, along with the relevant LUMO and HOMO for archetypical electron donors such as ethene and dimethylsulfide.

It is seen that the three computation methods agree concerning the relative ordering of energy levels of the given MOs.²⁴ The dioxirane LUMO lies in the molecular plane, and it has the

(24) For an excellent discussion about the qualitative use of Kohn–Sham orbitals to rationalize chemical phenomena, see: Stowasser, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1999**, *121*, 3414.

Table 3. Energy Levels (eV) Computed for the Significant Molecular Orbitals (MO) of Dimethyldioxirane (**1a**) and of Methyl(trifluoromethyl)dioxirane (**1b**)^a as Compared with Those of Performic Acid, Ethene, Acrylonitrile, and Dimethylsulfide

Entry	MO	DFT ^b	PM3	HF ^c	
1		LUMO	-0.48	-0.16	6.54
			-1.43	-1.23	5.55
2		HOMO	-7.12	-12.3	-12.5
			-8.03	-13.2	-13.6
3		LUMO (+1) ^d	-0.40	0.22	6.04
4		HOMO	-8.05	-12.0	-12.9
5		LUMO	0.52	1.23	5.01
6		HOMO	-7.26	-10.6	-10.2
7		LUMO	-1.53	-0.19	2.80
8		HOMO	-7.87	-10.9	-10.8
9		HOMO	-5.90	-8.88	-9.09
10		HOMO (-1)	-8.44	-11.4	-11.8

^a Values for TFDO (**1b**) are given in boldface. ^bB3LYP/6-31G(d). ^cHF/6-31G(d). ^dPeracid $\sigma^*(\text{O}-\text{O})$; the lower lying peracid LUMO (-0.63 eV, DFT) is a π^* pertaining to the carbonyl moiety.

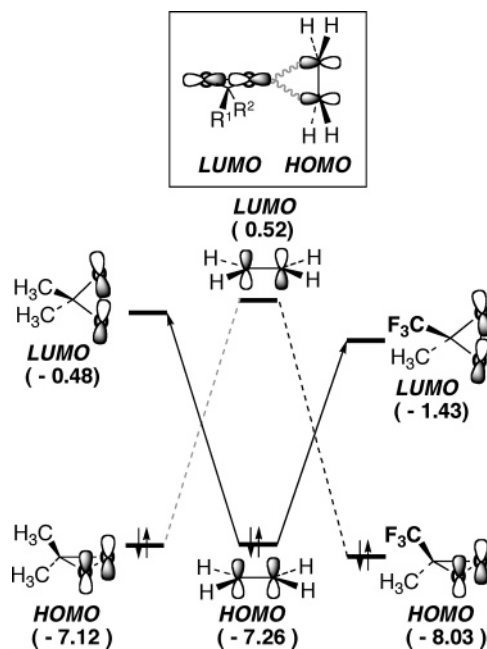
proper symmetry to interact with the alkene π bond.^{4f,7,12} By analogy to the typical HOMO–LUMO interaction drawn in S_N2 -type displacements on peroxide O–O bonds, the *dominant* orbital interaction involved in nucleophilic attack on the dioxirane should be the alkene π molecular orbital with the empty dioxirane O–O σ^* Walsh-type orbital.⁷

Thus, while the dioxirane oxygen lone pair's interaction with the alkene LUMO favor a spiro geometry in the TS, the alkene HOMO interacts in a stabilizing manner with the dioxirane LUMO (Chart 2). The same should hold true for powerful σ - or n -electron donor nucleophiles, such as dimethylsulfide.

The diagram in Chart 2 illustrates the fact that the TFDO epoxidations benefit by a lower HOMO (alkene)/LUMO (dioxirane) energy gap with respect to that of DDO.

Based on the MO energies given in Table 3, the same applies if the dioxirane epoxidation of the electron-poor acrylonitrile is considered. The major stabilization occurring on the way to the activated complex should give rise to a sizable difference in TS energies, hence to energy barriers of epoxidation significantly lower for TFDO as compared to DDO. Within this framework, it is seen that the lower lying HOMO of acrylonitrile (-7.87 eV) makes it a substrate substantially more reluctant than ethene to epoxidation by both DDO and TFD. This ordering

Chart 2. Relevant HOMO–LUMO Interaction for the Electrophilic Oxygen Transfer from Dioxiranes **1a,b** to Ethene^a



^a Energies (eV) estimated by B3LYP/6-31G(d) calculations.

appears to be in line with experimental findings.²⁵ Further inspection of data in Table 3 (entries 1–3) suggests that, based on LUMO energy levels, the TFDO oxidizing power is well above that of both performic acid and DDO by ca. 23 kcal mol^{-1} (1.03 eV). This again agrees with the experimental findings for reactions in the condensed phase, which strongly suggests that TFDO is best tailored for carrying out the electrophilic epoxidation of electron-poor substrates.^{4d,5}

In conclusion, the claim of a “biphilic” character of dioxirane reactivity¹² could not be substantiated by experiments. In fact, rate data herein unequivocally show that dioxiranes epoxidize electrophilically even with alkenes carrying electron-withdrawing groups. For epoxidation of electron deficient olefins, peracids can be as effective as dioxiranes; in analogy to the well-known Weitz-Scheffer epoxidation using alkaline hydrogen peroxide,^{26a} a two-step *nucleophilic* epoxidation avenue is open for the reaction of peracids with electron-poor olefins.²⁶ Thus, while the electrophilic/nucleophilic dichotomy for peracids as epoxidation reagents is amply supported *experimentally*, for dioxiranes this does not apply.

Along with high-level calculations concerning TS structure and energies, we deem that a simple FMO analysis is also useful

- (25) It should be mentioned that the energy barriers both from experiments and from computations should diminish markedly on going from gas to condensed phase. For instance, an *experimental* E_a of $8.0 \text{ kcal mol}^{-1}$ at 25°C (ΔH^\ddagger of $7.4 \text{ kcal mol}^{-1}$) has been measured for the DDO epoxidation of cyclohexene in an acetone solvent (ref 4c). The E_a values of 11.4 and $10.7 \text{ kcal mol}^{-1}$ have been estimated for the DDO epoxidation of cyclohexene in CHCl_3 and acetone, respectively, using the COSMO solvent mode [B3LYP/6-311+G(d,p)] (ref 7). The increased reactivity in polar solvents might be attributed to enhanced polarization of the TS relative to reactants; theoretical solvation studies are consistent with these observations (Jenson, C.; Liu, J.; Houk, K. N.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1997**, *119*, 12982); a systematic study of the effects of solvation and hydrogen bonding was also carried out by Gandolfi et al. at the B3LYP/6-31G(d) level (ref 23).
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in explaining the high reactivity of dioxiranes as electrophilic oxidants, based on the key stabilizing interaction nucleophile HOMO with dioxirane LUMO. In fact, both the LUMO of both the DDO (−0.43 eV) and of the TFDO (−1.43 eV) are energetically much more accessible to the nucleophile electron pair than the corresponding σ^* LUMO of classical peroxides.²⁷

Experimental Section

Materials and Methods. Boiling points and melting points were not corrected. The HPLC analyses were run using a Supelcosil ABZ+plus, 5 μm column (15 cm \times 4.6 mm id). Column chromatography was performed using silicagel (230–400 mesh), eluent *n*-hexane/ CH_2Cl_2 ; GC/MS experiments were run using a ZB-1 column (30 m \times 0.25 μm id), the MS detector in EI mode (70 eV). The ^1H NMR spectra were recorded on a 500 MHz or 400 MHz instrument; resonances are referenced to residual isotopic impurity (7.26 ppm) of CDCl_3 solvent and/or to TMS. The ^{13}C NMR spectral data (125.76 or 100 MHz) are referred to the middle peak of CDCl_3 solvent (77.0 ppm). FTIR spectra were run on samples in KBr pellets or films (KBr plates).

Commercial 1,1,1-trifluoro-2-propanone (TFP) (bp 22 °C) was purified by fractional distillation over granular P_2O_5 , stored over 5 Å molecular sieves, and routinely redistilled prior to use. Acetone and other solvents were purified by standard methods. Caroat triple salt $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ (a gift from Peroxid-Chemie, Degussa, Germany) was our source of potassium peroxomonosulfate employed in the synthesis of dioxiranes.³ Commercial tetrabutylammonium hexafluorophosphate ($\text{Bu}_4\text{N}^+\text{PF}_6^-$, purity >99%) was used in the cyclic voltammetry experiments.

Commercial (*E*)-*p*-methoxycinnamionitrile (**4a**), (*E*)-cinnamionitrile (**4c**), and (*E*)-*p*-chlorocinnamionitrile (**4d**) were further purified to >98% (HPLC) by standard techniques. (*E*)-*p*-Methyl-cinnamionitrile (**4b**),^{28a} (*E*)-*m*-chlorocinnamionitrile (**4e**),^{28a} and (*E*)-*m*-nitrocinnamionitrile (**4f**)^{28a} were synthesized by standard procedures upon conversion of commercially available cinnamic acids into corresponding amides, followed by treatment of the latter with P_2O_5 ; column chromatography afforded the nitriles above at $\geq 98\%$ purity (HPLC). The (*Z*)-*p*-methyl-cinnamionitrile (**4b'**)^{28b} and (*Z*)-cinnamionitrile (**4c'**)^{28b} were obtained upon photoisomerization^{28a} of the corresponding *trans*-stereoisomer and purified by column chromatography. All substrates gave physical constants and spectra (NMR, FTIR, GC-MS) in full agreement with literature.²⁸

Employed as an inert internal standard in HPLC runs, methyl 2,3,4,5,6-pentafluorobenzoate ($\text{C}_6\text{F}_5\text{CO}_2\text{Me}$, PFMB)²⁹ was obtained as a colorless liquid from the corresponding acid upon esterification with MeOH/BF_3 ;^{29b} it was purified by fractional distillation (bp: 44 °C/4 mmHg,^{29a} purity $\geq 98\%$, HPLC). Commercial tetrabutylammonium hexafluorophosphate ($\text{Bu}_4\text{N}^+\text{PF}_6^-$, TBAP) (purity 98%) was employed as the supporting electrolyte in cyclic voltammetry runs.

Solutions of 0.8–1.0 M methyl(trifluoromethyl)dioxirane (**1b**) in 1,1,1-trifluoropropanone (TFP) or in CCl_4 (ketone-free)^{3d} and solutions of 0.08–0.16 M dimethyldioxirane (**1a**) in acetone were made available upon adopting procedures, equipment, and precautions already reported in detail.³ The solutions were assayed for dioxirane content by iodometry and/or using a GC method after quenching the oxidant with excess *p*- $\text{MeC}_6\text{H}_4\text{SMe}$, which is rapidly and quantitatively oxidized to the corresponding sulfoxide.³ Authentic samples of the epoxides **5a–f** were synthesized upon reaction with dioxiranes **1a** or **1b** according to

a general procedure reported below and purified by column chromatography (purity $\geq 98\%$, HPLC). The following procedures are representative for the epoxidations of the alkenes above using dioxiranes.

Epoxidation of (*E*)-Cinnamionitrile (4c**) with Dimethyldioxirane (**1a**).** To a stirred solution of (*E*)-**4c** (19.4 mg, 0.15 mmol) in acetone (1 mL) at 25 °C, containing 0.1 M PFMB internal standard, was added in one portion a standardized cold solution of DDO (**1a**) in acetone (33 mL, 0.09 M, 3.00 mmol). The reaction progress was monitored by HPLC (acetonitrile/methanol/water; flow rate: 1.0–1.3 mL/min; detector, $\lambda = 220$ nm). Upon completion of the reaction (30 h, conv. >90%), the solvent was removed under reduced pressure and the residue was purified by column chromatography. The epoxide (*E*)-**5c** (yield >95%, purity $\geq 98\%$ HPLC) gave physical and spectral data identical to those of an authentic sample.^{30a,b}

Epoxidation of (*E*)-Cinnamionitrile (4c**) with Methyl(trifluoromethyl)dioxirane (**1b**).** To a stirred solution of (*E*)-**4c** (12 mg, 0.093 mmol) in acetone (4 mL) at 0 °C, containing 0.05 M PFMB internal standard, was added in one portion a standardized cold solution of TFDO (**1b**) in acetone (0.3 mL, 0.88 M, 0.28 mmol). The reaction progress was monitored by HPLC. Upon completion of the reaction (30 min, conv. >98%), the solvent was removed under reduced pressure and the residue was purified by column chromatography. The epoxide (*E*)-**5c** (yield >95%, purity $\geq 98\%$ HPLC) gave physical and spectral data identical to those of an authentic sample.^{30a,b}

(*E*)-3-(4-Methoxy-phenyl)-oxirane-2-carbonitrile (**5a**): colorless oil, bp 155–158 °C/6 mmHg (lit.^{30a} 105–114 °C/0.28 mmHg). (*E*)-3-(4-Methyl-phenyl)-oxirane-2-carbonitrile (**5b**):^{30a} colorless oil. (*Z*)-3-(4-Methyl-phenyl)-oxirane-2-carbonitrile (**5b'**):^{30a} colorless oil. (*E*)-3-Phenyl-oxirane-2-carbonitrile (**5c**):^{30a} colorless liquid, bp 135–137 °C/16 mmHg (lit.^{30b} 133–134 °C/16 mmHg). (*Z*)-3-Phenyl-oxirane-2-carbonitrile (**5c'**):^{30a} white solid, mp 55.5–56 °C (lit.^{30c} 55–57 °C). (*E*)-3-(4-Chloro-phenyl)-oxirane-2-carbonitrile (**5d**):^{30a} white solid, mp 67–68 °C (lit.^{30a} 68–69 °C). (*E*)-3-(3-Chloro-phenyl)-oxirane-2-carbonitrile (**5e**):³¹ white solid, mp 59–61 °C. (*E*)-3-(3-Nitro-phenyl)-oxirane-2-carbonitrile (**5f**):³² white solid, mp 118–120 °C.

Kinetics. Relative rates were determined under pseudo-first-order conditions, with the dioxirane in large excess (from 20- to 80-fold) over initial concentrations of the alkenes. The procedure used was based on the amount of starting material consumed during the kinetic run. At zero time a thermostatted aliquot (20 to 2 mL) of standard acetone solution of dioxirane **1a** (0.07–0.09 M) or of dioxirane **1b** (0.6–0.9 M, in TFP) was added to an acetone solution (also thermostatted) containing the two given alkene substrates (*A* and *B*, usually 0.01–0.04 M for **1a** and 0.003–0.008 M for **1b**) competing for the oxidant, as well as the internal standard PFMB. Over the initial 15–50% reaction, aliquots (0.2–1 mL) were withdrawn periodically and quenched with 0.3 mL of 0.5 M *p*- $\text{MeC}_6\text{H}_4\text{SMe}$ in acetone. The relative rates were determined from the concentration percentage of alkenes remaining, $[A]/[A]_0$ and $[B]/[B]_0$. The chromatogram area of the alkenes was corrected for the detector response, determined separately for each cinnamionitrile substrate using standard solutions of the alkene containing the internal standard. Relative rate coefficients were estimated as $k^A/k^B = \log([A]/[A]_0)/\log([B]/[B]_0)$.

In each experiment, at least two values were measured at various reaction times; data from two or more independent runs were averaged (estimated error: $\leq 10\%$).

Absolute rates of DDO oxidations were determined at 25.0 ± 0.1 °C under pseudo-first-order conditions, with the alkene substrate in large excess (from 20- to 50-fold) over the dioxirane initial concentra-

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tion. At zero time, an aliquot (10–20 mL) of a thermostated solution of dioxirane **1a** ($(0.55\text{--}0.81) \times 10^{-2}$ M) was added to 180 mL of $(4.6\text{--}7.2) \times 10^{-2}$ M solution of the alkene in acetone (also thermostated). The decrease of dioxirane concentration with time was measured by iodometric titrations of aliquots (10 or 20 mL) periodically withdrawn from the reaction flask. Plots $\log[a_0/(a_0 - x)]$ vs time, linear to over 50% reaction, yielded the pseudo-first-order k_1 (s^{-1}) value; from this, and the known alkene initial concentration, k_2 ($\text{M}^{-1} \text{s}^{-1}$) values were estimated. Data agreeing within $\pm 10\%$ were averaged.

Absolute rates of TFDO oxidations were determined at 5.0 ± 0.1 °C under second-order conditions, with initial concentrations of both reagents ranging 0.015–0.05 M. At zero time, an aliquot (5 mL) of a dioxirane **1b** thermostated solution (0.240–0.280 M) was added to a 0.05–0.06 M solution of the alkene in acetone. The decrease in the dioxirane concentration was determined by iodometry of aliquots (5 mL or 10 mL) periodically withdrawn from the reaction solution. Integrated second-order rate plots $\log[b(a-x)/a(b-x)]$ vs time were linear to over 70% reaction, yielding the k_2 ($\text{M}^{-1} \text{s}^{-1}$) value. Based on two or more independent runs, data agreeing within $\pm 10\%$ were averaged.

Cyclic Voltammetry. The CV experiments were run using an EG&G-PAR 273 potentiostat/galvanostat controlled by a universal programmer. A plotter was used to record the current voltage output at 200 mV/s sweep rate. A conventional three-electrode system consisting of a glassy carbon working electrode (od 3 mm), a platinum wire counter electrode, and a saturated calomel reference electrode (SCE) were employed. All electrochemical measurements were carried out at 20 °C in the same solvent, i.e., dry acetonitrile, thus avoiding problems related to liquid-junction potentials. Commercial tetrabutylammonium hexafluorophosphate ($\text{Bu}_4\text{N}^+\text{PF}_6^-$, TBAP) ca. 0.1 M served as the supporting electrolyte. Aliquots of mother solutions that was either 0.08 M DDO in acetone or 0.2 M TFDO in CCl_4 ^{3d} were used to prepare ca. 2×10^{-3} M dioxirane solutions in dry acetonitrile.

The DDO solutions were carefully deoxygenated by bubbling an Ar gas stream through them for at least 10 min prior to recording of the voltammetric data; instead, TFDO solutions could be only partially freed by atmospheric oxygen by the mentioned procedure since it was found that the inert gas stream depletes substantially the solution of this volatile dioxirane species.³ The potential scan range was from –3.0 to +1.0 V vs SCE, allowing us to estimate the electron reduction potentials ($E_{\text{p}}^{\text{cat}}$) of TFDO and of DDO as shown in Figure 1.

Computational Methods. All calculations were carried out using the Gaussian 2003 suite of programs.³³ High-level computations by Bach et al. (as well as by other authors) have demonstrated that the B3LYP variant of DFT calculations is a useful method and accurate enough for studying dioxirane and peroxyacid epoxidations;⁷ accordingly, we employed the B3LYP method for full geometry optimizations both in the gas phase and in solution. Solvent effects were evaluated with the self-consistent reaction field (SCRF) theory using the PCM-united atom topological model (UAHF, radii of interlocking spheres obtained through the Barone's HF parametrization) as implemented in

the C.02 version of Gaussian 2003. The dioxirane reduction to the give the corresponding radical anion was studied by using the 6-311++G-(2d,p) basis set of triple ζ quality with diffuse and polarization functions, which is appropriate in describing molecules bearing functionalities rich in lone pairs, such as the peroxide moiety^{7,23} as well as anionic systems. At first, a geometry optimization of DDO and TFDO in acetone or acetonitrile was performed; then, the dioxirane radical anion energy was estimated by single-point calculations on the geometries attained in each of the solvents above. Regarding epoxidations of ethene or acrylonitrile either by DDO or by TFDO, the somewhat smaller basis set 6-31+G(2d,p) was employed; in fact, we recently reported that the latter computational method is quite appropriate to describe peracid epoxidations, nicely reproducing the results achievable using much larger basis sets.^{23e} All stationary points were confirmed by vibrational frequency analysis (i.e., one imaginary frequency was found for all TSs). The two gas-phase TSs relative to the reaction of ethene with DDO and TFDO were found stable with the keyword stable=opt. Concerning the case of the TSs of reactions of DDO and of TFDO with acrylonitrile in the gas phase, the stability test revealed a small RHF-UHF instability (0.6 kcal/mol and $S^2 = 0.25$ for DDO's TS; 0.34 kcal/mol and $S^2 = 0.19$ for TFDO's TS), which might suggest a small diradical character for these transition structures. For the reaction of DDO with acrylonitrile, we located two TSs (respectively, *exo* and *endo*), of which just the *exo* one (carrying the cyano group on the side opposite to the dioxirane alkyl groups) is given in Figure 2. Actually, the two TSs above exhibit the same energy in acetone. Similarly, of the four TSs located in the reaction of TFDO with acrylonitrile, just the *exo,anti* structure is presented; again, the energies of the TSs omitted were found to be quite close to that of the TS represented in Figure 2. Charge transfer (CT) data were estimated from NPA charges. CHELPG calculations gave slightly different values, confirming electron donation from the alkenes to dioxiranes.

Acknowledgment. Partial support of this work by the National Research Council of Italy (CNR) is gratefully acknowledged. Thanks are due to professor F. Magno and his staff (Department of Analytical Chemistry, University of Padova, Italy) for help in running and interpreting the cyclic voltammetry experiments. We are pleased to dedicate this work to professor F. Naso (University of Bari, Italy) and to professor W. Adam (Emeritus, University of Puerto Rico) on the occasion of their 70th birthday.

Supporting Information Available: Experimental details, supplemental characterization data, and sample HPLC data for substrates and products. Energy of dioxiranes and dioxirane radical anions at the B3LYP/6-311++G(2d,p) level (acetone and acetonitrile solution), energy and Cartesian coordinates of all TSs at the B3LYP/6-31+G(2d,p) level (gas phase and solution). Imaginary frequency for all TSs. Complete ref 33. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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