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Mechanistic Significance of *Perepoxide Trapping* Experiments, with Epoxide Detection, in $^1\Delta_g$ Dioxygen Reactions with Alkenes

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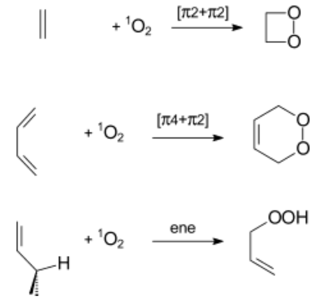
Received October 29, 2002

The reactions of $^1O_2$ with alkenes can share open-chain diradicals or cyclic peroxiranes as common polar intermediates. The latter in particular has been postulated on the basis of trapping experiments, which exploit the capability of reducing agents (R) to extract an oxygen atom from the putative perepoxide, to generate an epoxide. This theoretical study illustrates that trapping experiments cannot distinguish between a peroxirane and an open-chain intermediate pathway, because an epoxide is the shared outcome of the attack by R.

Introduction

Dioxygen, in its first excited degenerate $^1\Delta_g$ state, is an important reactive species in oxidation reactions.[1,2a] It is generated in the troposphere by ozone photolysis,[2b,3] and in the oxidation and combustion of hydrocarbons.[2c,4] While $^1\Delta_g$ O_2 has proved useful in organic synthesis,[2a] its reactions with some biomolecules have been inspected,[2d] thus determining that it is capable of damaging organic tissues and attacking DNA bases.[5] This species reacts in different modes with organic unsaturated molecules,[6−8] and the three more common reactions are displayed in Scheme 1: the [π2+π2] and [π4+π2] cycloadditions, and the *ene*[9] (or Schenck)[10,11] reaction, which is a group transfer reaction.[6b]

SCHEME 1



The mechanisms of these three reactions are interrelated by the possibility of sharing some short-lived intermediate, and different reaction mechanisms have been recommended on account of experimental data relevant to a variety of molecular systems.[7,8] Some evidence in favor of the existence of nonconcerted pathways in the ene and [π2+π2] reactions (Scheme 2) has been collected,[6c] which could see the involvement either of open-chain polar diradical/zwitterionic intermediates[11] or of a peroxirane.[12] This kind of cyclic intermediate (also called perepoxide) was first proposed by Sharp.[13] Then, evidence in favor of its intervention was presented in a kinetic isotope effect (KIE) study.[14] Also more recent stereochemical studies and KIE experiments,[15−19] concerning the ene reaction,[20] have yielded results which are

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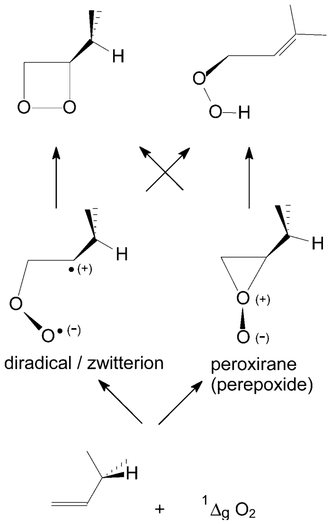
SCHEME 2



often (but not always) best accommodated by putting forward the intermediacy of peroxirane, or a peroxirane-like exciplex. By contrast, some recent theoretical studies, though carried out undeniably on simple systems, have provided indications in support of open-chain diradical intermediates. Two recent CAS-MCSCF and CAS−PT2 studies on ethene, methyl vinyl ether, and butadiene[21] and on ethenol[22] have found that peroxiranes are energy minima, nonetheless attainable only by passing through the corresponding polar diradicals (a carbon−oxygen diradical has some zwitterionic character).[11] A diradical intermediate was also found in a recent CAS-MCSCF and CAS-MC-QDPT2 study of the [π4+π2] cycloaddition of singlet oxygen to butadiene.[23] Also a very recent theoretical study on the ene reaction of $^1\Delta_g$ O$_2$ with propene, carried out in this laboratory,[24] confirms the involvement of a polar diradical intermediate, while a peroxirane, though stable, is not representative of a viable pathway.

Experiments have been devised in the past to intercept intermediates in singlet dioxygen reactions, by exploiting the capability of some reducing agents (R)[25] as the sulfoxides,[26,27] sulfides,[27] phosphites,[28,29,31] or sulfenate and sulfinate esters,[30] to extract an oxygen atom from the unknown intermediate. In some cases, an epoxide and the oxidized form of R were detected, and the intermediacy of a perepoxide maintained.[25,26,28−30] In two of the studies[28,30] it was established, by way of Hammet studies, that the attack by P- or S-centered reducing agents had definitely an electrophilic nature.

The present theoretical study points out that trapping experiments are unable to differentiate between an open-chain intermediate pathway and a peroxirane intermediate pathway, because generating an epoxide is the common outcome of the attack by the reducing agent on either species.

Method

The stable and transition structures were determined by gradient procedures[32] within the Density Functional Theory (DFT), and making use of the B3LYP functional.[33] This functional is of widespread use, and even if prone to underestimate some reaction barriers, it has generally performed well as regards geometries and energetics. The polarized 6-311G(d,p) basis set[34] was used in the DFT(B3LYP) optimizations. Then the nature of the critical points was checked by diagonalization of the 6-311G(d,p) analytic Hessian (vibrational analysis). The more extended 6-311+G(2df,p) basis set[34] was used for the final single-point energy calculations. As already noted in previous studies, the unrestricted DFT monodeterminantal wave function for diradicals has to be handled in a manner already described[21,24] to get a qualitatively correct picture in terms of nonzero spin densities, and the energy values so obtained need to be refined by using the formula suggested by Yamaguchi.[35] The final corrected DFT-(B3LYP)/6-311+G(2df,p)//6-311G(d,p) energies were then combined with the 6-311G(d,p) thermochemical corrections from the vibrational analysis to get estimates of the activation and reaction enthalpies and free energies.[36]

The relevant enthalpy and free energy differences are collected in Table 1. A more complete set of energies, enthalpies, and free energies is presented (together with the relevant critical point geometries) as Supporting Information.

The DFT calculations were carried out by using the GAUSSIAN 98 system of programs.[37] The two transition structures

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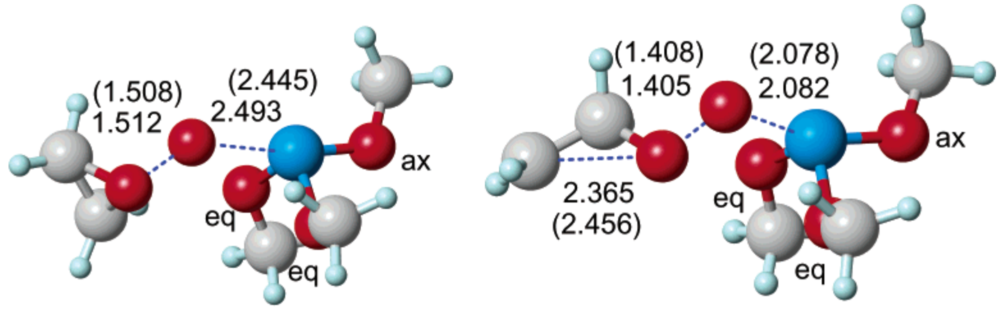
TABLE 1. Estimates of the Relative Enthalpy and Free Energy Differences (at 298 K) for the Reactions Involving Ethene and *cis*-But-2-ene[a]

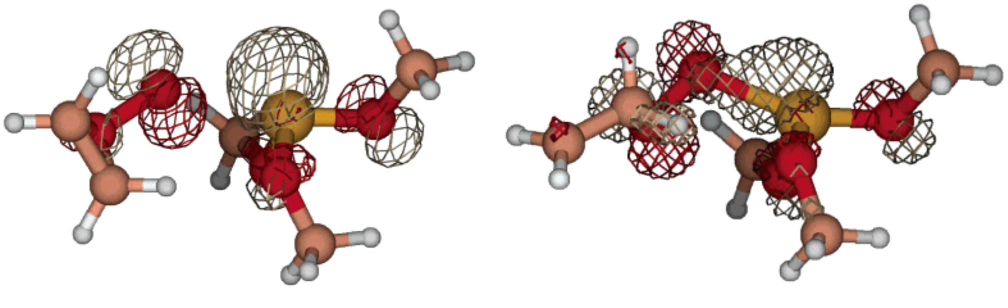
		ethene		*cis*-but-2-ene	
structure		ΔH	ΔG	ΔH	ΔG
peroxirane + $P(OCH_3)_3$	**1**	9.4	11.2	5.8	7.5
interconversion TS + $P(OCH_3)_3$	**TS 1-2**	13.2	15.0	9.8	10.7
peroxyl diradical + $P(OCH_3)_3$	**2**	0.0	0.0	0.0	0.0
O abstraction TS from **1**	**TS 1-3**	7.7	21.3	4.3	17.7
O abstraction TS from **2**	**TS 2-3**	5.8	17.2	8.8	20.7
epoxide + O = $P(OCH_3)_3$	**3**	−128.0	−125.4	−128.6	−125.8

[a] DFT(B3LYP)/6-311+G(2df,p)//6-311G(d,p) energies, combined with the 6-311G(d,p) thermochemical corrections for H and G (units: kcal mol^{-1}).



TS 1-3 **TS 2-3**

FIGURE 1. Transition structures for the terminal oxygen atom (O′) transfer from the perepoxide (**TS 1-3**) or the open-chain polar diradical (**TS 2-3**) to the phosphorus-centered reducing agent. Only those of the ethene system are displayed, as those of the *cis*-butene system are similar. The reported interatomic distances (in angstroms) make reference to the dashed bonds; those relevant to the *cis*-butene system are in parentheses.



a **b**

FIGURE 2. TS for O′ transfer in the ethene system. (a) The HOMO of the perepoxide + phosphite **TS 1-3**. (b) The next-highest occupied α orbital of the peroxyl diradical + phosphite **TS 2-3**; the beta is very close in shape, and is not displayed. The two highest occupied α and β orbitals are those typical of a diradicaloid structure. Similar plots are obtained for the *cis*-butene system. The phosphorus lone pair orbital is mixed with one O′ lone pair p-type orbital.

shown in Figure 1 are drawn by the MolMol 2.4 program,[38a] while the MO plots in Figure 2 are drawn by the Molden program.[38b] The more important optimum interatomic distances reported in them are in ångströms.

Results and Discussion

The intermediates possibly generated by singlet dioxygen attack onto ethene (initially chosen as a simple model system) and to *cis*-but-2-ene are considered. Thus, the results pertaining to the gas-phase O-abstraction reactions operated by $P(OCH_3)_3$ onto the ethene perox-

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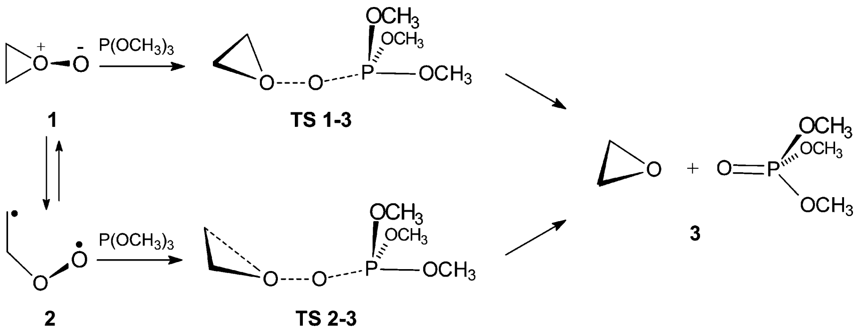
SCHEME 3



irane (or *cis*-but-2-ene peroxirane) and the corresponding open-chain peroxyl diradicals are presented and discussed in this section.

Scheme 3 sketches (for ethene) how the two different intermediates can interconvert and undergo oxygen abstraction by passing through two distinct transition structures (**TS 1-3** and **TS 2-3**), through which they finally converge on the same products, ethene (or *cis*-but-2-ene) oxide and trimethyl phosphate, **3**.

As already discussed in a preceding paper,[21] in the simple ethene + $^1O_2$ model system the peroxyl diradical is the lowest energy intermediate. The peroxirane intermediate, which can be attained only by passing through the diradical, is higher in energy by ca. 8 kcal mol^{-1}. The related ΔH and ΔG values (at 298 K), referred to the peroxyl diradical**,** are collected in Table 1. As substitution of one to four hydrogens of the ethene model substrate by methyl groups, to get more complex alkenes, places the peroxirane higher in energy than the diradical by 5−12 kcal mol^{-1} (and susbtitution by a single methoxy group by 5),[21,39] the two intermediates could be thought of as being able to interconvert to some extent (Scheme 3), more so if the effect of a polar medium is considered. In fact, a Polarizable Continuum Method (PCM)[40] simulation of the solvated ene reaction of propene and singlet dioxygen (in acetonitrile) brings about a differential stabilization of the propene perepoxide with respect to the polar diradical of ca. 4 kcal mol^{-1}.[39]

The O-abstracting agent can initially give some interaction complexes with these two intermediates. For ethene, the peroxirane-P(OCH$_3$)$_3$ complex is at $\Delta E = -4.7$ kcal mol^{-1} with respect to the relevant separate moieties (but at $\Delta G = 6.8$ kcal mol^{-1}), and the diradical-P(OCH$_3$)$_3$ complex is at $\Delta E = -0.8$ kcal mol^{-1} with respect to the corresponding separate moieties (but at $\Delta G = 8.7$ kcal mol^{-1}). The actual role of these complexes (already dubious on the energy hypersurface, as the reacting system could circumvent the relevant energy dips and go through the oxygen atom abstraction) seems to be negligible in terms of free energy, as the depressions associated with the complex geometries are no longer present (see Figure 3). For this reason there has been no search for the corresponding complexes involving *cis*-butene.

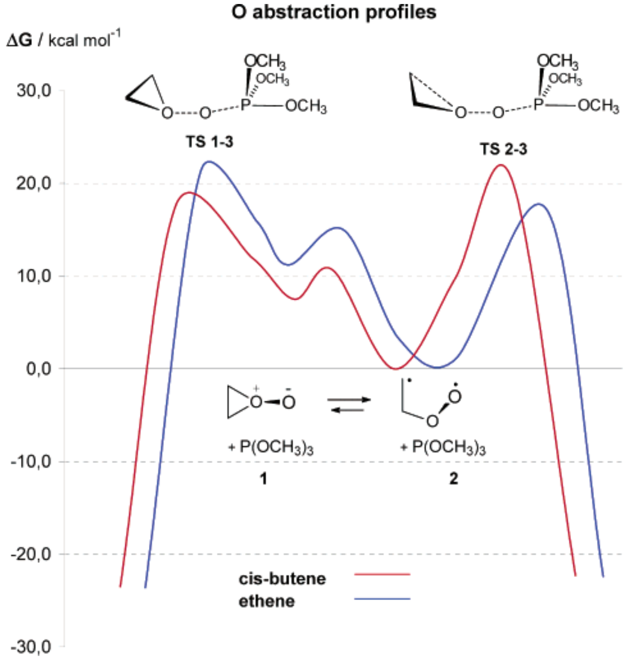


FIGURE 3. Free energy profiles for the oxygen atom transfer from the ethene (blue line) and *cis*-butene (red line) perepoxides (via **TS 1-3**) or from the relevant open-chain polar diradicals (via **TS 2-3**) to the trimethyl phosphite reducing agent, with final production of an epoxide (and trimethyl phosphate) in both cases (products not shown).

O-Abstraction from the perepoxide or from the open-chain polar diradical goes through transition structures whose geometrical features are displayed in Figure 1. The terminal oxygen atom O′ moves from the perepoxide in **TS 1-3**, or from the open-chain polar diradical in **TS 2-3**, to the phosphorus of the trimethyl phosphite reducing agent. As can be evinced from the O′PO angles, the arrangement of the oxygens around P is not far from trigonal bipyramidal. These angles are 169, 90, and 90° wide for **TS 1-3**, and 158, 95, and 96° wide for **TS 2-3**. So, the transferred oxygen O′ and one methoxy oxygen are almost axial (O_{ax}), and the other two methoxy oxygens almost equatorial (O_{eq}). The P lone pair occupies the remaining quasiequatorial position, as illustrated by the HOMO of **TS 1-3** in Figure 2a. These features, shared by the two transition structures, hint at an electrophilic character of the attack of phosphorus onto the terminal oxygen, possibly with some involvement of the phosphorus empty valence d orbitals, and concurrent minimization of the destabilizing interaction between the P lone pair and those of O′ (the HOMO of **TS 1-3** in Figure 2a is their higher energy out-of-phase combination).[41] The electrophilic character of the attack by P- or S-centered reducing agents was indeed demonstrated by the Ham-

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(40) Cammi, R.; Tomasi, J. *J. Chem. Phys.* **1994**, *100*, 7495−7502 and references therein.

met studies reported in refs 28 and 30. It is also consistent with the electronic distribution calculated for the reactant trimethyl phosphite, in which the electron density of the phosphorus atom is depleted, due to the electron-withdrawal capability of the methoxy oxygens.[42] One could imagine in the two transition structures the beginning of an interaction preluding to the new pπ−dπ bond present in the hypervalent product trimethyl phosphate. Yet, making reference to the reactants, unsignificant flows of charge between the two components come about in the two transition structures, and a noteworthy role of the d(P) orbitals as electron acceptors cannot be evinced from the electron population analysis. These aspects could be consistent with the earliness of the transition structures suggested by the large exoergicity (Table 1), and by the geometrical parameters. In fact, the O−O′ bond is stretched only by 3% (**TS 1-3**) or 7% (**TS 2-3**) in either system; the O−P distance is still larger than that in the final product by 68% (**TS 1-3**) or 41% (**TS 2-3**) in either system again.

Inspection of the higher energy filled orbitals of the reactants as well as on the transition structures suggests that the P atom does not have any role as nucleophile.

Table 1 shows that O-abstraction from the perepoxide is described as rather easy for both alkenes: $\Delta G^{\ddagger} \approx 10$ kcal mol^{-1} in terms of free energy, with reference to the perepoxide itself (free energy differences will be discussed in the following). The same process in the polar ethene diradical is more demanding ($\Delta G^{\ddagger} \approx 17$ kcal mol^{-1}). However, if we consider that the ethene perepoxide is less stable than the relevant diradical by 11 kcal mol^{-1} (and can form in addition only from it),[**21**] the overall barrier for the ethene perepoxide pathway is higher than that for the diradical pathway by 4 kcal mol^{-1} (Figure 3, blue line). On the other hand, in *cis*-butene the perepoxide is somewhat less than 8 kcal mol^{-1} above the diradical, and the O-abstraction process from the latter is less easy than that for ethene ($\Delta G^{\ddagger} \approx 21$ kcal mol^{-1}). Therefore, in this case, the overall barrier for the diradical pathway is slightly higher than that for the perepoxide pathway, by 3 kcal mol^{-1} (Figure 3, red line).

As the terminal oxygen atom gets abstracted from the diradical in **TS 2-3**, the ensuing exceedingly easy spin coupling in the latent $H_2C^{\bullet}-CH_2-O^{\bullet}$ diradical causes a new C−O bond to form. The ring closure and exoergic collapse (ca. −125 kcal mol^{-1}) to the corresponding epoxide requires no activation altogether, and characterizes that part of the reaction pathway that lies past the TS. This is evident on the basis of an IRC study carried out with **TS 2-3** as origin (see the Supporting Information). A persuading animation based on the IRC log file can be seen from the program Molden.[38b] Moreover, a geometry optimization, looking for a minimum and starting from the same TS, brings about the same result. In fact, this second event is hardly hinted at in the transition structure: the involved C and O atoms are slightly closer than in the diradical, but only by a small percent of the overall distance change. Therefore, two events come about in a highly asynchronous manner, yet the overall process is concerted.

The concertedness of the O-abstraction/epoxide ring closure process in the open-chain intermediate is a key result of the present computational study, and points out that trapping experiments, though producing a clear experimental result, have to be interpreted with some caution as regards the nature of the intercepted intermediate.

Conclusions

The intermediacy of a peroxirane in the ene and [π2+π2] cycloaddition reactions of singlet dioxygen with alkenes has been put forward also on the basis of trapping experiments. These are carried out by exploiting the capability of certain reducing agents of extracting an oxygen atom from the putative perepoxide, to generate an epoxide. This study (in which trimethyl phosphite has been chosen as a representative electrophilic reducing agent) points out that such an experiment cannot demonstrate in a compelling way the intervention of a peroxirane, because an identical result is obtained by abstraction of the terminal oxygen atom from an open-chain polar diradical intermediate (zwitterion).

Acknowledgment. Financial support has been provided by the Italian MURST (now MIUR), within the Programma di Ricerca Scientifica di Rilevante Interesse Nazionale “Chimica in Fase Gassosa di Specie Reattive Neutre e Cariche”, 2001.

Supporting Information Available: A listing of geometries, total energies, enthalpies, and free energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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[41] Compare: Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1985; Chapter 14, pp 269−276.

[42] The Natural Atomic Orbital (NAO) charges were computed, within a Natural Bond Orbital (NBO) analysis, at the B3LYP/6-311+G(2df,p)//B3LYP/6-311G(d,p) level. These NAO charges are the following: +1.57 (P); −0.84 (O); +0.32 (CH_3). The last two figures are average values over the three methoxy groups. NBO analysis: Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735−746. Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066−4073. Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211−7218.