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Transition structures for one step nonconcerted oxygen insertion mechanism of oxidation of alkanes with trifluoroperoxyacetic acid

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Abstract—High level calculations (UB3LYP/6-31G*) on the oxygen insertion by trifluoroperoxyacetic acid (TFPA) into methane and isobutane C–H bonds strongly supports the viability of a one step nonconcerted mechanism. That is, the O–H bond forms first and the C–O bond formation commences afterwards, but only one first order saddle point, exhibiting high diradical character and strong polarization, is present on the energy profile of the minimum energy path. No minima corresponding to intermediates were located. IRC analysis suggests that the transition structure can collapse directly to products with retention of configuration at the alkane carbon center. © 2001 Elsevier Science Ltd. All rights reserved.

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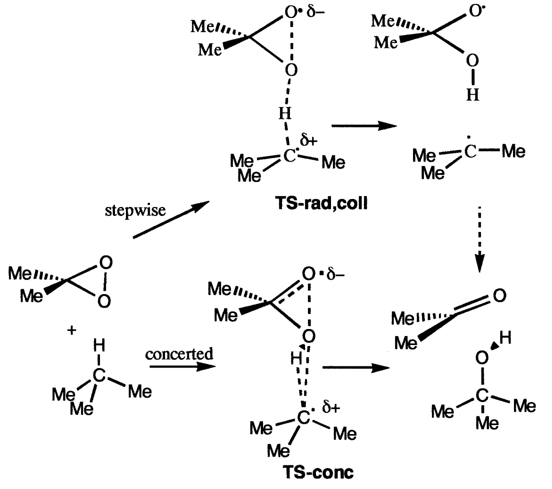
1. Introduction

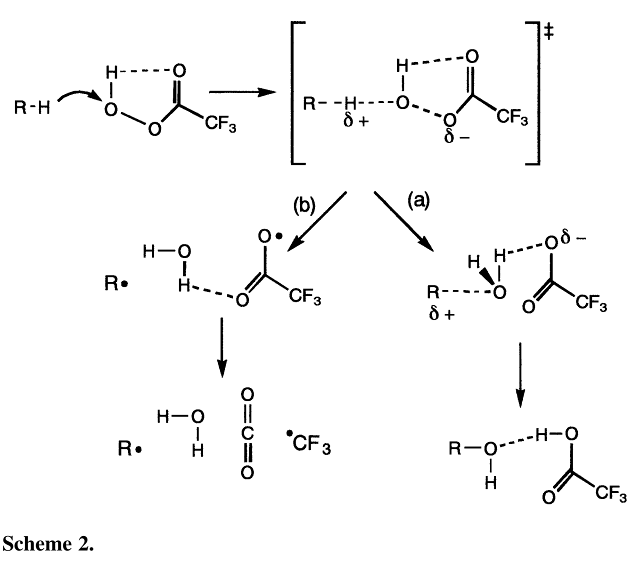
Oxygen insertion into C–H bonds by a variety of oxidants[1] and catalytic systems[2] leads to formation of related hydroxy derivatives as primary products and has attracted much experimental attention owing to the intrinsic high synthetic relevance of the selective oxidation of hydrocarbons. Different mechanisms have been advanced with a resultant interesting and stimulating debate about the most controversial points.



Scheme 1.

In the case of the synthetically useful hydroxylation of alkanes by dioxiranes (Scheme 1)[3,4] and peracids (Scheme 2)[5,6] the mechanistic debate among experimentalists has been centered on 'concerted oxenoid insertion vs stepwise molecule induced homolysis' or 'non-radical vs radical' controversy.

Three high level computational studies on the reaction of dioxiranes with alkanes by Houk's,[7] Bach's[8] and Rauk's[9] groups, using restricted DFT methods, located transition structures (e.g. **TS-conc**, Scheme 1) that can be classified as concerted, since they can collapse directly to final products. However, these TSs show high diradical character and strong polarization. Successively we located, using



Scheme 2.

Keywords: transition structures; nonconcerted oxygen insertion; trifluoroperoxyacetic acid.

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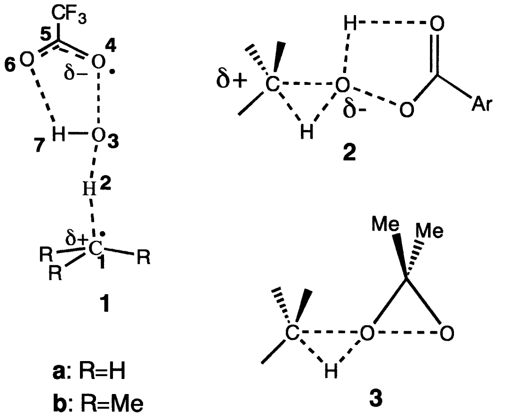


Scheme 3.

restricted and unrestricted DFT methods, two types of alternative TSs, diradicaloid in nature, (one of them, **TS-rad,coll**, is depicted in Scheme 1) that can lead to final products via radical pair intermediates.[10] Concerted TSs can easily explain the most noteworthy experimental data such as the complete retention of configuration of the alkane center involved in dioxirane oxygen insertion reaction. However, these TSs suffer from an RHF→UHF instability that does not allow one to definitively accept them as genuine TSs.[11] The diradical stepwise pathways, although energetically feasible and with true 'stable' TSs, seem to be less convincing in explaining experimental observations.

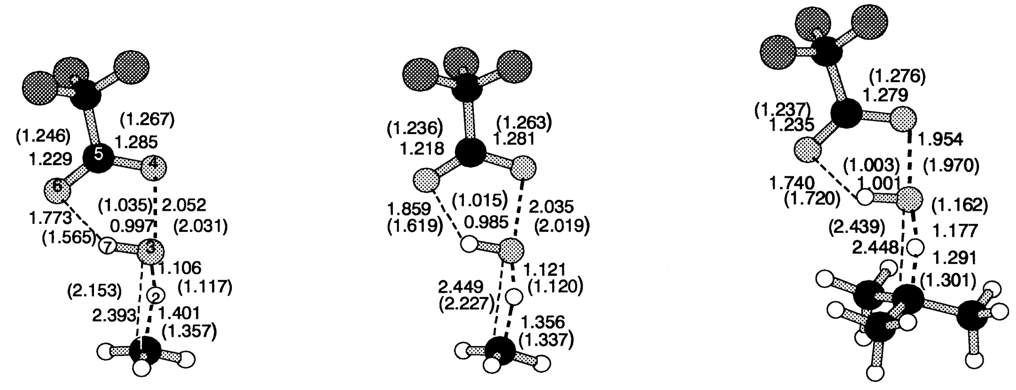
Rauk further suggested that **TS-conc** can be common to both concerted insertion and radical pair formation, as a result of bifurcation after the saddle point.[9]

In addition, the reaction of alkanes with peracids show experimental evidence for both radical and concerted mechanisms. Very recently Camaioni[5a] suggested that the mechanism of alkane oxidation with trifluoroperoxyacetic acid (TFPA) is analogous to Rauk's hypothesis for dioxirane hydroxylation, that is, after the TS (see Scheme 2) the reaction pathway divides into two channels: along the first one (a) the system develops zwitterionic character and collapses to products with configuration retention while along the other one (b) the radical character prevails leading to a radical pair that, on escaping from the cage, can trigger radical chain reactions.

No computational data have been produced to date of the mechanism for the reaction of peroxy acids with alkanes, thus the paper by Camaioni et al. prompted us to disclose our B3LYP computational results on the reaction of trifluoroperoxyacetic acid with methane and isobutane. Our data demonstrate that TSs for these reactions must be depicted as in TS **1** (Scheme 3) while a representation such as that in TS **2** (the TS suggested for concerted oxenoid insertion mechanism)[5b] is wrong.

2. Computational methods

All calculations were performed with the Gaussian 98 suite of programs.[12] The geometry optimization for all stationary points were performed by using the hybrid density B3LYP functional[13] and the 6-31G* basis set. Owing to the possible radical character of the species along the reaction pathway both the restricted and unrestricted B3LYP methods have been used. The R(U)B3LYP TSs, with relevant bond lengths (Å), are displayed in Fig. 1 while further geometric



U-1a (R-1a) **U-1a′ (R-1a′)** **U-1b (R-1b)**

Figure 1. DFT optimized geometries (lengths in Å) for TSs of methane and isobutane hydroxylation by TFPA.

Table 1. Angles (°), dipole moments (D) and CHelpG charges for the TSs of the TFPA hydroxylation of methane and isobutane at the B3LYP/6-31G* (**1a** and **1b**) and B3LYP/6-311+G** level (**1a′**)

	C_1–H_2–O_3	C_1–O_3–O_4	H_7–O_3–O_4–C_5	μ	CHelpG Charges		
					Alkyl	$H_2O_3H_7$	$O_4C_5(CF_3)O_6$
R-**1a**	120.7	171.5	0.9	6.05	0.15	0.27	−0.42
R-**1a′**	129.8	172.1	0.3	6.84	0.16	0.28	−0.44
R-**1b**	163.8	173.6	0.6	7.78	0.39	0.01	−0.40
U-**1a**	145.0	172.2	1.1	4.96	0.11	0.18	−0.29
U-**1a′**	162.9	177.4	0.6	5.86	0.15	0.16	−0.31
U-**1b**	165.6	175.1	0.5	7.39	0.37	0.01	−0.38

data are given in Table 1 (see **1** in Scheme 3 for TS numbering). The nature of stationary points (minima or transition structures (TS)) have been verified by diagonalizing the Hessian matrices calculated for the optimized structures. Transition structures had only one negative eigenvalue (first order saddle points) while ground state structures showed only positive values. The wave function stability was checked for all the first order saddle points and wave functions of the RB3LYP/6-31G* TSs proved to be sligtly unstable (see Section 3). The harmonic vibrational frequencies were also calculated and used unscaled[14] to provide the zero point vibrational energy (ZPE) and the contribution of molecular motions to enthalpy, entropy and free energy (at 298.15 K).

The TS for the methane reaction was fully optimized also at the R(U)B3LYP/6-311+G** level (**1a**′ in Fig. 1) and similar electronic activation energies were obtained also from single point R(U)B3LYP/6-311+G** calculations on R(U)B3LYP/6-31G* geometries. For the isobutane reaction energy refinement was performed only by single point calculations [R(U)B3LYP/6-311+G**//R(U)B3LYP/6-31G*] on the lower level geometries.

The contribution of solvent effects to the activation free energy were calculated with the CPCM model (as implemented in Gaussian 98) which includes the non electrostatic terms (cavitation, dispersion and repulsion energy) in addition to the classical electrostatic contribution.[15] The solvation effect has been evaluated for dichloromethane solution[16] by single point calculation (i.e. with unrelaxed gas-phase reactant and TS geometries) at the B3LYP/6-31G* level and used to evaluate both the B3LYP/6-31G*, B3LYP/6-311+G**//B3LYP/6-31G* and B3LYP/6-311+G** solution free energies.

Electronic energies and activation parameters (gas phase and solution) from R(U)B3LYP/6-31G* and R(U)B3LYP/6-311+G**//R(U)B3LYP/6-31G* calculations for methane and isobutane reactions and from R(U)B3LYP/6-311+G** optimizations for methane reaction are reported in Table 2.

To ensure that TSs connect reactants and products we have performed intrinsic reaction coordinate (IRC) calculations at the UB3LYP/6-31G* level for both the alkane ractions and the most representative IRC points for the isobutane reaction are depicted in Fig. 2.

3. Results and discussion

Exploration of the potential energy surface of the reaction of trifluoroperoxyacetic acid with methane and isobutane, using the RB3LYP/6-31G* method, led us to locate transition structures R-**1a** and R-**1b** (Fig. 1), respectively, for the oxygen insertion in these two hydrocarbons. Both these TSs exhibit a low RHF→UHF instability (0.01 and 0.05 kcal/mol, respectively, for R-**1a** and R-**1b**) that certainly are a reflection of the diradical character of both TSs.[17] This observation indicates that a more proper description of these reactions should be obtained by unrestricted DFT methods. Calculations with the UB3LYP/6-31G* method gave rise to 'genuine' first order saddle points (U-**1a** and U-**1b**) whose energy is very similar (lower by 0.86 and 0.04 kcal/mol, respectively) to that of R-**1a** and R-**1b**. In the case of isobutane reaction not only the energy but also the geometry of the UB3LYP/6-31G* TS differs almost negligibly from that of the RB3LYP/6-31G* TS (e.g. C_1–H_2–O_3 angle is 164° in R-**1b** and 166° in U-**1b**). Variations for the TS geometry of methane reaction are more pronounced: on passing from R-**1a** to U-**1a** there is a considerable widening of the C_1–H_2–O_3 angle (i.e. C_1–H_2–O_3 angle is 121° in R-**1a** and 145° in U-**1a**) with a considerable increase (of 0.24 Å) in the O_3–C_1 distance. To corroborate this latter finding we studied the methane reaction also with the R(U)B3LYP/6-311+G** method. Once again the restricted wave function was RHF→UHF unstable (by 0.1 kcal/mol) and there are significant geometry changes on going from the 'restricted' (R-**1a**′) to the 'unrestricted' structure (U-**1a**′) (e.g. C_1–H_2–O_3 angle is 130° and 163° and O_3–C_1 distance is 2.227 Å and 2.449 Å in R-**1a**′ and U-**1a**′, respectively).

Thus, the oxygen insertion mechanism by peroxy acids into alkane C–H bonds can be confidently discussed on the basis of TS U-**1** (U-**1a**, U-**1a**′ and U-**1b**) as they are true (stable with only one imaginary frequency) transition structures.

The activation free energy obtained in gas phase with the UB3LYP/6-31G* method (Table 2) does not change

Table 2. Activation parameters for TFPA insertion into alkane C–H bonds from fully B3LYP/6-31G* (**1a** and **1b**) and B3LYP/6-311+G** (**1a**′) optimizations and from single point B3LYP/6-311+G**//B3LYP/6-31G* calculations in gas phase and in dichloromethane ($\Delta G^{\neq}{}_{\text{sol}}$) solution

B3LYP optimizations							B3LYP/6-311+G**//B3LYP/6-31G*		
Structure	E	$\Delta E^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$	$\Delta G_{\text{sol}}{}^{\neq}$	$\Delta E^{\neq}$	$\Delta G^{\neq}$	$\Delta G^{\neq}{}_{\text{sol}}$
R-**1a**	−642.361217	38.1	35.9	−19.4	41.7	39.8	32.1	35.6	33.7
R-**1a**′	−642.589652	32.1	29.9	−19.3	35.6	34.2			
R-**1b**	−760.327308	22.0	19.4	−20.0	25.4	24.5	15.5	18.8	18.0
U-**1a**	−642.362581	37.3	34.0	−15.7	38.7	38.2	31.1	32.5	32.0
U-**1a**′	−642.591629	30.9	27.0	−13.9	31.2	30.7			
U-**1b**	−760.327373	22.0	19.0	−18.9	24.6	24.1	15.7	18.4	17.9

B3LYP/6-31G*: energies in kcal/mol, entropy in cal/mol K (Symmetry number (σ) used to calculate entropy are 12 for methane, 3 for isobutane and 1 for all TSs); standard state (298.15 K) of the molar concentration scale (gas in ideal mixture at 1 mol/L, P=1 atm).[14] Energies (kcal/mol) for methane is −40.518383, isobutane is −158.458814, and TFPA is −601.903612. B3LYP/6-311+G**: energies (kcal/mol) for methane is −40.533928; and TFPA is −602.106918. Single point B3LYP/6-311+G**//B3LYP/6-31G* calculations: energies (kcal/mol) for methane is −40.533914, isobutane is −158.506398, TFPA is −602.106639, R-**1a** is −642.589466, R-**1b** is −760.588313, U-**1a** is −642.590959, and U-**1b** is −760.587942). For evaluation of the thermodynamic properties the B3LYP/6-31G* computed kinetic contributions are used. ($\Delta G^{1}{}_{\text{sol}}$): solvent (dichloromethane) effect according to CPCM model at the B3LYP/6-31G* level.

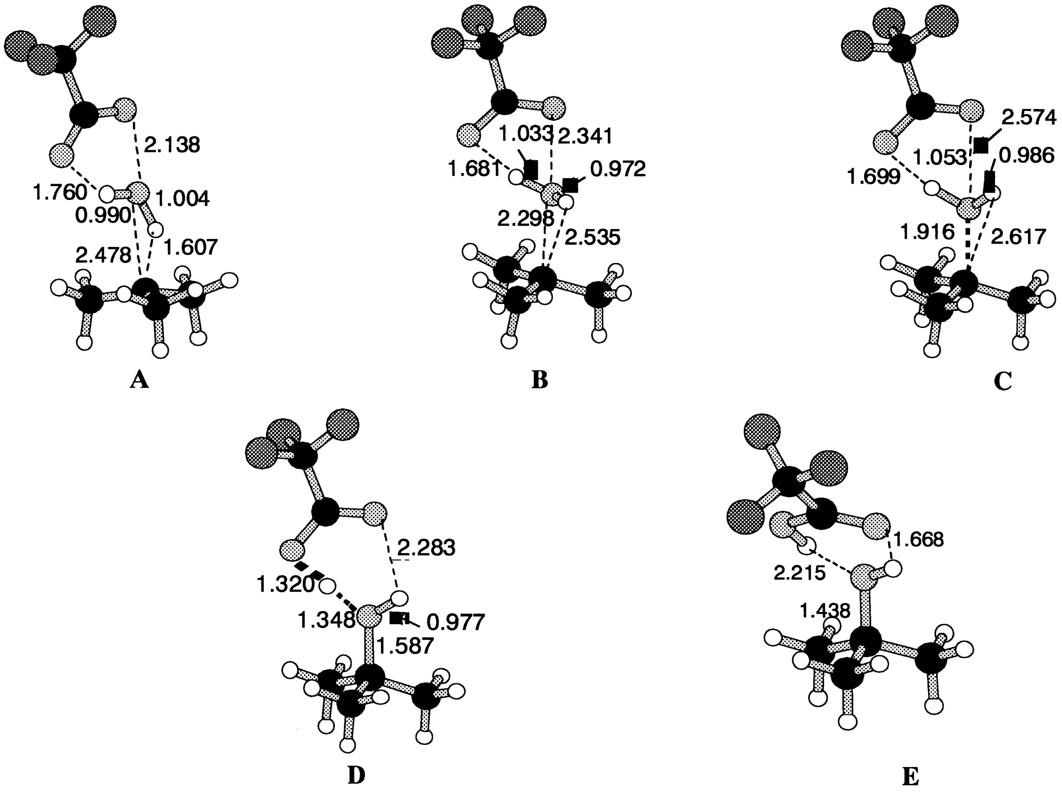


Figure 2. Representative UB3LYP IRC points for the isobutane reaction with TFPA (bond lengths in Å).

appreciably when solvation effects (dichloromethane as solvent) are introduced with the CPCM model, indicating that electrostatic solvation factors do not play an important role in this reaction. The theoretical activation free energy looks somewhat too high if one compares the value of 24 kcal/mol calculated for the reaction of the isobutane tertiary C–H bond with that reported for cyclohexane secondary C–H bond (≈22 kcal/mol in TFA at 25°C).[5a] Energy evaluation with a larger basis set (6-311+G**), both by full optimizations and by single point calculations on lower level geometries, strongly decreases the activation free energy. In the case of the isobutane reaction it is lowered from 24 to 18 kcal/mol (Table 2) that sounds as a more reasonable figure.[18]

Even a quick inspection of the TSs U-**1a** (U-**1a′**) and U-**1b**, shown in Fig. 1, clearly reveals that these TSs are quite different from the 'oxenoid insertion mechanism' (**2** in Scheme 3) proposed by some authors for these reactions.[5b] The latter mechanism suggests that formation of the two new bonds occurs in concert and, in particular, that considerable bonding between O_3 and C_1 is operative in the transition structure whereas the geometry of calculated transition structures **1** stands in contrast with this suggestion. In fact, the distance between O_3 and C_1 ($\geq$2.39 Å) and the C–H–O alignment ($<C_1–H_2–O_3=145°$ in U-**1a** and ≈165° in U-**1a′** and U-**1b**) demonstrates that O_3–C_1 bonding interaction is actually very small while the H transfer from C_1 to O_3 is well advanced (incipient $O_3–H_2\leq1.18$ Å). The breaking C_1–H_2 bond is loosely aligned with the breaking O_3–O_4 bond and practically lies in the TPFA plane.

The diradicaloid character of TSs U-**1a** and U-**1b** is testified by the spin density at C_1 (0.55 and 0.14, respectively) and O_4 (−0.51 and −0.18, respectively) centers while the $\langle S^2\rangle$ value (0.46 and 0.05 for the methane and isobutane reactions, respectively) tells us that their wave function does not describe a pure singlet state but is slightly contaminated by triplet character.[19] The attack by the peroxyacid on alkane is electrophilic and the resultant sizeable electron transfer from the latter to the former brings about a strong polarization of the TSs U-**1a** and U-**1b** as documented by the net atomic charges on the alkyl moiety (+0.11 and +0.37, respectively) and the high dipole moments (4.96 D and 7.39 D, respectively). Thus, it seems that the introduction of methyl groups brings about a consistent decrease of the diradical character of the TS (i.e. spin density on C_1 and O_4 and $\langle S^2\rangle$ value in U-**1b** are notably lower than in U-**1a**) paralleled by enhancement in the zwitterionic character. Interestingly, on the basis of CHelpG charges, TS U-**1b** can be viewed as two charged moieties (*t*-butyl, positively charged, and trifluoroacetate, negatively charged) with some radical character separated by a neutral water molecule (Table 1).

IRC following, starting from U-**1b**, on one side led to isobutane and trifluoroperoxyacetic acid, demonstrating that TSs **1** can originate directly from reactants, and on the other side terminates with isobutanol and trifluoroacetic acid. Following the IRC path toward products is quite enlightening (Fig. 2). In the first part of the descent there is an increase in the diradical character of the system, as documented by the strong increase of spin density at C_1 (from 0.14 for TS U-**1b** to 0.50 for IRC point **A**) and O_4 (from −0.18 for TS U-**1b** to −0.44 for **A**) centers and also by the relevant enhancement of spin contamination present in the wave function of **A** ($\langle S^2 \rangle$=0.43) in comparison to that of U-**1b** ($\langle S^2 \rangle$=0.05). Continuing along the descent, the diradical character disappears while polarization strongly increases (net positive charge on the alkane moiety=0.53 and net negative charge on trifluoroacetate moiety=0.70) and there is a rotation of the 'water molecule' to afford **B** that looks like a solvent separated ion pair (t-Bu$^+$/H_2O/CF_3COO^-). Water rotation is certainly driven by the tendency to optimize electrostatic interactions. The system **B** is held together by the water molecule through hydrogen bonding (to the trifluoroacetate moiety) and electron pair donation (to the carbocationic tertiary center). The following steps (**C**–**E**) correspond to formation of the protonated alcohol (C_1–O_3=1.92 Å at point **C**) and back donation of proton to the trifluoroacetate anion (e.g. **D**, where the interaction of H_7 with O_3 and O_6 are almost the same) to produce the hydrogen bonded complex between isobutanol and trifluoroacetic acid (**E**).

Camaioni et al. in their qualitative representation of this mechanism, have skillfully suggested most of the characteristics that we have now corroborated with calculations.

These authors also suggest a bifurcation that should originate at the TS **1**. Apparently, IRC point **A**, with high radical character, seems more appealing as a starting point for a bifurcation that leads to water separated radical pair in alternative to the water separated ion pair path. However, to date we did not manage to uncover any evidence for this bifurcation.

As obvious as it might be, we feel that it is important to emphasize that the pathway disclosed by our calculations corresponds to a reaction channel that leads to products with configuration retention at the alkane center, through what looks like a 'nonconcerted' (as far as the timing of the new bonds (i.e. C_1–O_3 and O_3–H_2) formation is concerned) TS followed by a diradical-like and a zwitterion-like species that however are not minima. That is, it represents a good example of *one step nonconcerted* mechanism.[21]

Retention of configuration does not necessarily require a concerted TS and the data reported earlier represents a computational confirmation that this may also happen in alkane hydroxylation with peroxyacids. In fact, at the TS, bonding between the attacking oxygen (O_3) of TFPA and the alkane mostly involves the transferring hydrogen atom H_2 while the alkane carbon C_1 is hardly significantly involved in bonding interaction with O_3, in particular in the case of **1b**.

These observations may, to some extent, also hold for 'concerted' TSs of oxygen insertion into C–H bond by dioxiranes. In fact, in TSs of type **conc** (Scheme 1) the transferring hydrogen interacts strongly with the inserting oxygen while the carbon–oxygen bonding interaction is, as can be inferred from computational data,[7–10] relatively weak. We are dealing with a one step concerted but highly asynchronous TS, that is, one can even speak of a borderline concerted–nonconcerted situation. Thus, qualitative structures like **3** (Scheme 3), that can be used to describe **conc** TSs for these reactions, should not be understood as indicating a strong interaction of the carbon center with the oxygen atom but (as far as one trusts computational data) only as schematically describing a mechanism that leads to final products with retention of configuration.

4. Conclusion

This paper reports UB3LYP/6-31G* calculations on the oxygen insertion by TFPA into methane and isobutane C–H bonds. These computational data provide appealing evidence in favor of the viability of a nonconcerted (with reference to the two new bond formation) reaction path that goes through a true first order saddle point, with significant diradical character and considerable polarization as well. In this transition structure the peroxyacid oxygen atom, bound to be inserted into the C–H bond, exhibits a considerable bonding interaction with the hydrogen atom while the carbon atom seems not to be significantly involved in bonding. Notwithstanding this feature, IRC analysis demonstrates that this TS can collapse directly to products, with retention of configuration at the alkane carbon center, that is, a one step nonconcerted[21] mechanism is operative.

Our data corroborate several aspects of a very recent mechanistic proposal advanced by Camaioni et al. for these reactions.

Acknowledgements

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molecular system exhibits an RHF⟶UHF instability (i.e. the restricted solution is unstable) it means that there is a lower energy wavefunction corresponding to the unrestricted solution (UB3LYP) of the SCF equation. As a consequence, the stable UB3LYP solution has to be used in order to get a reliable description of the energetics and geometric data of the molecular system under study. For a recent discussion about this topic see: Grafenstein, J.; Hjerpe, A. M.; Cremer, D.; Kraka, E. *J. Phys. Chem.* **2000**, *104*, 1748–1761.

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16. Oxygen insertion by peroxy acids has been carried out both in dichloromethane and in TFA. Since CPCM model cannot describe specific solvation factors such as hydrogen bonding we have chosen dichloromethane as solvent to have a clue to the solvent effect in particular to electrostatic effects.
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18. The experimental activation free energy has been evaluated from kinetic data, by Camaioni et al. on TFPA–cyclohexane reaction. Secondary hydrogens of cyclohexane should be definitely less reactive (even including statistical factors) than the tertiary ones of isobutane. Some uncertainty in kinetic experimental data (owing to the complexity of the reaction mechanism as a result of the putative competing (a) and (b) pathways (Scheme 2)) and the fact that they have been measured in a solvent such as TFA impedes us to reliably judge which of the two computational figures is closer to the actual free activation energy.
19. A problem for the unrestricted methods is that wave functions for the optimized singlet open-shell species exhibit spin contamination, that is, wave functions are not pure singlet but contain a triplet component. This drawback seriously affects UHF calculations but seems to be much less important for DFT methods. The low $\langle S^2 \rangle$ values for TSs under study suggest that their singlet wave functions contain a small amount of the triplet component and this moderates to a large extent the effect of the considerable (≈17 kcal/mol for U-**1a**) singlet–triplet energy gap (with the former always more stable) in increasing the calculated energies. Given that it has not been definitely established whether and how UB3LYP energies of spin contaminated wave function has to be corrected, we did not perform energy correction by removing spin contamination. This might mean that the true energy of diradicaloid TSs described in this paper is lower (by ≈5 kcal/mol in the case of U-**1a**)[11,20] than the reported values.
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21. Concertedness is not a uniquely defined concept. According to Williams, the most universally accepted definition, that has the particular merit to enable unambiguous diagnosis of what is concerted or nonconcerted, is as follows 'a concerted mechanism has no intermediates and thus possesses only a single transition state'.[22] Thus, in the light of this definition the oxygen insertion described in this paper must be labeled as concerted. However, according to Lowe 'the word concerted is meaningless unless we state what the two processes (the reference processes) are that occur simultaneously' and when 'one process takes place first and the second one commences afterwards' the mechanism must be labeled nonconcerted.[23] Consequently, the process under study is 'nonconcerted' as far as the timing of O–H and C–O bond formation is concerned. Calculations of transition structures and of IRC paths provide a detailed description of bond changes during a reaction making it possible to label a mechanism as one step nonconcerted (in addition to the more obvious cases of one step concerted and stepwise nonconcerted processes) thus conveying reliable and useful information both on the potential energy profile of the minimum energy pathway (as advocated by Williams) and on the timing of two reference processes (as considered mandatory by Lowe).
22. Williams, A. *Chem. Soc. Rev.* **1994**, 93–100.
23. Lowe, J. P. *J. Chem. Educ.* **1974**, *51*, 785–786.