Inorg. Chem. **2007**, 46, 7992–7997

Inorganic Chemistry
Article

O–O Bond Cleavage in Dinuclear Peroxo Complexes of Iron Porphyrins: a Quantum Chemical Study

Margareta R. A. Blomberg,* Adam Johannes Johansson, and Per E. M. Siegbahn

Department of Physics, Stockholm University, S-106 91 Stockholm, Sweden

Received April 16, 2007

To gain insight into the mechanisms of O_2 activation and cleavage in metalloenzymes, biomimetic metal complexes have been constructed and experimentally characterized. One such model complex is the dinuclear peroxo complex of iron porphyrins observed at low temperature in a noncoordinating solvent. The present theoretical study examines the O–O bond cleavage in these complexes, experimentally observed to occur either at increased temperature or when a strongly coordinating base is added. Using hybrid density functional theory, it is shown that the O–O bond cleavage always occurs in a state where two low-spin irons ($S = \pm^1/_2$) are antiferromagnetically coupled to a diamagnetic state. This state is the ground state when the strong base is present and forms an axial ligand to the free iron positions. In contrast, without the axial ligands, the ground state of the dinuclear peroxo complex has two high-spin irons ($S = \pm^5/_2$) coupled antiferromagnetically. Thus, the activation barrier for O–O bond cleavage is higher without the base because it includes also the promotion energy from the ground state to the reacting state. It is further found that this excitation energy, going from 10 unpaired electrons in the high-spin case to 2 in the low-spin case, is unusually difficult to determine accurately from density functional theory because it is extremely sensitive to the amount of exact exchange included in the functional.

I. Introduction

The biological importance of the transport and activation of molecular oxygen by iron complexes has generated a research area dedicated to the study of biomimetic iron complexes and their reactions with O_2. Several of the most important biological iron complexes involved in the binding and reduction of oxygen, such as myoglobin, cytochrome P450, and cytochrome *c* oxidase, contain porphyrin ligands. The target for many studies has therefore been the interaction of molecular oxygen with different types of iron porphyrin complexes. One purpose of studying biomimetic iron complexes is to gain a better understanding of the process of reduction of molecular oxygen, thereby elucidating, for example, the mechanisms of O_2 reduction in respiration; see further the review by Kim et al. on synthetic models of heme-copper oxidases.[1]

In a recent study, Karlin and co-workers[2] studied the reactivity of $(F_8TPP)Fe^{II}$ with molecular oxygen, where F_8TPP = tetrakis(2,6-difluorophenyl)porphyrinate(2−). Of special interest are the results obtained at reduced temperature in the noncoordinating solvent dichloromethane, where a stable diporphyrin peroxo complex is irreversibly formed; see Figure 1. It was observed that if a nitrogenous base, such as 4-(dimethylamino)pyridine (DMAP), was added to the cold solution of the already formed diporphyrin peroxo complexes, the O−O bond was immediately cleaved and a new species, assigned as a six-coordinated, high-valent $Fe^{IV}{=}O$ (ferryl) complex, appeared. Similar results have been obtained previously by Balch and co-workers for the interaction of molecular oxygen with different iron porphyrin complexes.[3−6]

In the present study, hybrid density functional theory (DFT) is used to examine the O−O bond cleavage reaction in dinuclear porphyrin peroxo complexes, particularly using the F_8TPP ligand. Comparisons will be made to experimental

---

* To whom correspondence should be addressed. E-mail: mb@physto.se.

[1] Kim, E.; Chufán, E. E.; Kamaraj, K.; Karlin, K. D. *Chem. Rev.* **2004**, *104*, 1077−1133.

[2] Ghiladi, R. A.; Kretzer, R. M.; Guzei, I.; Rheingold, A. L.; Neuhold, Y.-M.; Hatwell, K. R.; Zuberbühler, A. D.; Karlin, K. D. *Inorg. Chem.* **2001**, *40*, 5754−5767.

[3] Chin, D.-H.; Del Gaudio, J.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1977**, *99*, 5486−5488.

[4] Chin, D.-H.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 4344−4350.

[5] Balch, A. L.; Chan, Y.-W.; Cheng, R.-J.; La Mar, G. N.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7779−7785.

[6] Balch, A. L. *Inorg. Chim. Acta* **1992**, *198−200*, 297−307.

10.1021/ic7007182 CCC: $37.00

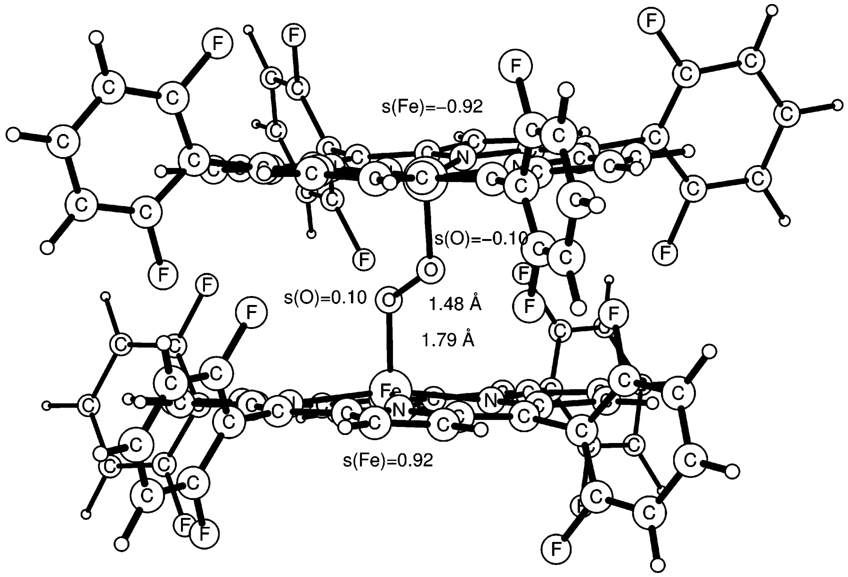

Figure 1. Optimized dinuclear iron peroxo complex, in the low-spin ($S = \pm{}^1/_2$) antiferromagnetic state. The most important interatomic distances and spin populations are given. The corresponding unsubstituted complex has the same structural parameters.

results for the reaction rate. The effect of the presence of a base will also be investigated.

II. Methods and Models

Quantum mechanical calculations have been performed on the porphyrin complexes employing the hybrid DFT B3LYP.[7−9]

The program *Jaguar 5.5*[10] was used to optimize molecular geometries at the B3LYP/lacvp level, and for the optimized structures, single-point calculations of the energy were performed at the B3LYP/lacv3p** level. lacvp[10] is a basis set of double-ζ quality, while lacv3p**[10] is of triple-ζ quality with polarization functions on all atoms. Both basis sets include an effective core potential for iron. The self-consistent reaction field method implemented in *Jaguar* was used to evaluate electrostatic solvation effects.[11,12] For the solvent dichloromethane, a dielectric constant $\epsilon = 9.1$ was used.

For the O−O bond cleavage reaction, approximate transition states were determined by constrained optimization at different O−O bond distances. For the smaller model complex, as described below, the structure of the approximate transition state was used in full transition-state optimizations with an explicitly calculated Hessian matrix, i.e., second derivatives of the energy with respect to the nuclear coordinates. The calculation of the Hessian matrices as well as the full transition-state optimizations were performed with the *Gaussian 03* package[13] using the same functional and basis set as those described above. The Hessians were also used to calculate zero-point and entropy effects.

Several benchmark tests on the accuracy of the B3LYP functional have been performed.[14] On the basis of those results, an average error of 3−5 kcal/mol is expected for the computed relative energies for transition-metal-containing systems.[15] There are indications that the reparametrized B3LYP* functional, which uses 15% Hartree−Fock exchange as compared to the 20% used in the original functional, gives a better description of the relative energies in transition-metal-containing systems.[16,17] Therefore, the B3LYP* functional has been used to check some of the relative energies discussed below.

The calculations were performed using the actual tetrakis(2,6-difluorophenyl)porphyrinate(2−) ligand (F_8TPP); see Figure 1. In order to evaluate the effects of the porphyrin substituents, some calculations were also performed using an unsubstituted porphyrin. For this model, full transition-state optimizations were performed, and Hessians were calculated to give thermal effects. It should be noted that the differences between the approximate transition states and the fully optimized ones were found to be insignificant. For the F_8TPP systems, which are too large for Hessian calculations, the thermal effects were taken from the corresponding unsubstituted system. The base 4-(dimethylamino)pyridine (DMAP) was modeled by 4-(dihydroamino)pyridine (DHAP). Test calculations showed that the effects of replacing the aminomethyl groups with hydrogens are negligible. For example, the calculated binding energies of the axial ligand to the ferryl−oxo complex were identical for the two models.

III. Results and Discussion

In this section, the results from the calculations will be presented and discussed. In the first subsection, possible spin states of both monomer and dinuclear iron porphyrin complexes are discussed. As it turns out, the dinuclear peroxo

---

(7) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098−3100. Becke, A. D. *J. Chem. Phys.* **1993** *98*, 1372−1377. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(8) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(9) Stephens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623−11627.

(10) *Jaguar 5.5*; Schrödinger, L.L.C.: Portland, OR, 1991−2003.

(11) Tannor, D. J.; Marten, B.; Murphy, R.; Friesner, R. A.; Sitkoff, D.; Nicholls, A.; Honig, B.; Ringnalda, M.; Goddard, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 11875−11882.

(12) Marten, B.; Kim, K.; Cortis, C.; Friesner, R. A.; Murphy, R. B.; Ringnalda, M.; Sitkoff, D.; Honig, B. *J. Biol. Chem.* **1996**, *100*, 11775−11788.

(13) *Gaussian 03*, Revision B.03; Gaussian Inc.: Pittsburgh, PA, 2003.

(14) Curtiss, L. A.; Raghavachari, K.; Redfern, R. C.; Pople, J. A. *J. Chem. Phys.* **2000**, *112*, 7374−7383.

(15) Siegbahn, P. E. M.; Blomberg, M. R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 221−249.

(16) Reiher, M.; Salomon, O.; Hess, B. A. *Theor. Chem. Acc.* **2001**, *107*, 48−55.

(17) Salomon, O.; Reiher, M.; Hess, B. A. *J. Chem. Phys.* **2002**, *117*, 4729−4737.

Table 1. Calculated Splittings between Different Spin States for Iron(II) Porphyrin Monomers[a]

$\mathrm{Fe^{II}}$ complex	axial ligand	$E(S{=}0)$ (kcal/mol)	$E(S{=}1)$ (kcal/mol)	$E(S{=}2)$ (kcal/mol)	exp.[b] ground state
Porf		+23.0 (23.2)	0	+3.6 (6.1)	
$\mathrm{F_8TPP}$		+23.4 (23.4)	0	+4.4 (6.7)	$S = 1$
$\mathrm{F_8TPP}$	pyridine	0	+8.6 (10.4)	+6.0 (11.7)	$S = 0$

[a] Values in parentheses refer to the B3LYP* results. [b] Reference 2.

complexes are unusually difficult to model. One of the reasons is that the reactions involve spin switches in two steps for two centers, yielding a 4-fold uncertainty in the computed spin splittings, as compared to the more common situation with one metal center and one step of spin switch. In the second subsection, the results for the O−O bond cleavage barrier are presented, and in the last subsection, comparisons are made to experimental results for the O−O bond cleavage.

IIIa. Spin States and Splittings. To accurately reproduce experimental splittings between different spin states of transition-metal complexes by quantum chemical calculations is a nontrivial issue. In particular, for iron(II) porphyrin complexes, it has been shown that different methods give different ordering of the spin states. For example, CASPT2 gives a quintet ground state for an unsubstituted iron(II) porphyrin,[18] while B3LYP and other DFT functionals give a triplet ground state, in agreement with experimental data for substituted porphyrins.[19,20] In the present study, calculations were performed on the different spin states of both $\mathrm{F_8TPPFe^{II}}$ and $\mathrm{PorfFe^{II}}$, where Porf denotes an unsubstituted porphyrin. The effect of pyridine axial ligands was also investigated. The results are summarized in Table 1. For the $\mathrm{F_8TPPFe^{II}}$ complex, the calculations yield a triplet ground state, in agreement with experimental results for the same complex in noncoordinating solvents.[2] The quintet state is found to be 4.4 kcal/mol higher in energy and the singlet state 23.4 kcal/mol higher. The singlet is an open-shell state, and it is therefore corrected using the Heisenberg−Hamiltonian formalism.[21] The closed-shell singlet state is at 31.1 kcal/mol. The calculations for the unsubstituted porphyrin complex show that the substituents have almost no effect on the spin splittings (less than 1 kcal/mol); see Table 1. In strongly coordinating solvents, like pyridine, the ground state is found to shift to the diamagnetic singlet state,[2] which is also reproduced by the calculations using DHAP as the axial ligand. The results are given for the six-coordinated complex. In the table, also results for the B3LYP* functional,[16] with only 15% HF exchange, are given. As can be seen, rather small effects are obtained from a decrease in the amount of exact exchange, as expected destabilizing high-spin states relative to lower spin. In no case is the computed ground state changed. These results show that the method used is reasonably reliable in this case.

Table 2. Calculated Energy Splittings between Different Antiferromagnetically Coupled States at the Equlibrium Structure of the Dinuclear Peroxo Complexes[a]

Fe ligand	axial ligand	$E(S{=}\pm{}^{1}/_{2})$ (kcal/mol)	$E(S{=}\pm{}^{3}/_{2})$ (kcal/mol)	$E(S{=}\pm{}^{5}/_{2})$ (kcal/mol)
Porf		13.5 (4.0)	7.0 (2.5)	0
Porf	DHAP	0		
$\mathrm{F_8TPP}$		16.0 (6.7)	8.7 (2.3)	0
$\mathrm{F_8TPP}$	DHAP	0		

[a] B3LYP* values are given in parentheses.

The most important spin states to be determined in the present context are concerned with the dinuclear peroxo complexes (Figure 1). In this case, two $\mathrm{Fe^{III}}$ ions are involved. Experimental information shows that the two iron ions are antiferromagnetically coupled in these peroxo complexes, yielding diamagnetic ground states.[4] In agreement with these observations, the calculations give the antiferromagnetic coupling of the two irons lowest in energy for all peroxo systems investigated. It should also be noted that in all cases the ferromagnetically coupled state is only slightly higher in energy (1−2 kcal/mol), and therefore the single determinant description, inherent in DFT, of the open-shell low-spin states should give reliable energies. On the other hand, there seems to be no experimental information about the spin state of the individual $\mathrm{Fe^{III}}$ ions in the peroxo complex, even if a high-spin coupling seems to be assumed.[4] Three different spin states of iron were considered in the calculations: high spin ($S = \pm{}^{5}/_{2}$), intermediate spin ($S = \pm{}^{3}/_{2}$), and low spin ($S = \pm{}^{1}/_{2}$), all coupled antiferromagnetically. For the $\mathrm{(F_8TPP)Fe{-}O{-}O{-}Fe(F_8TPP)}$ complex, the high-spin irons gave the lowest energy, with the intermediate-spin irons 7.3 kcal/mol above, and the low-spin irons 16.0 kcal/mol above; see Table 2. However, these splittings are quite sensitive to the amount of exact exchange, and using the B3LYP* functional, the high-spin to low-spin iron splitting changes from 16.0 to 6.7 kcal/mol. This result indicates an unusually large uncertainty in the computed spin splitting, and the reason is that there are two metal centers, both recoupling the spin in two steps ($S = \pm{}^{5}/_{2}$ to $\pm{}^{1}/_{2}$). Similar results for the state splittings are found for the unsubstituted complex, PorfFe−O−O−FePorf, where the intermediate-spin iron state lies 9.0 kcal/mol above and the low-spin iron state 13.5 kcal/mol above the high-spin iron ground state, using the normal B3LYP functional. When a strong base, DHAP, is added to the empty iron positions in the peroxo complex (see Figure 2), the calculations show that the state with two low-spin irons ($S = \pm{}^{1}/_{2}$) becomes by far the lowest state. In fact, it was not possible to converge to a true peroxo state with high spin on both irons with the base ligand present.

Finally, for the $\mathrm{Fe^{IV}{=}O}$ product of the O−O bond cleavage, the calculations give the triplet state as the ground state in all cases, which is in agreement with experimental information for both the five- and six-coordinated systems.[5]

IIIb. O−O Bond Cleavage in the Peroxo Complex. The target of the present study is the O−O bond cleavage process, starting from the dinuclear peroxo complexes. It should be

---

(18) Pierloot, K. *Mol. Phys.* **2003**, *101*, 2083−2094.

(19) Kozlowski, P. M.; Spiro, T. G.; Bérces, A.; Zgierski, M. Z. *J. Phys. Chem. B* **1998**, *102*, 2603−2608.

(20) (a) Rovira, C.; Ballone, P.; Parrinello, M. *Chem. Phys. Lett.* **1997**, *271*, 247. (b) Rovira, C.; Kunc, K.; Hutter, J.; Ballone, P.; Parrinello, M. *J. Phys. Chem. A* **1997**, *101*, 8914.

(21) Noodleman, L.; Case, D. A. *Adv. Inorg. Chem.* **1992**, *38*, 423−470.

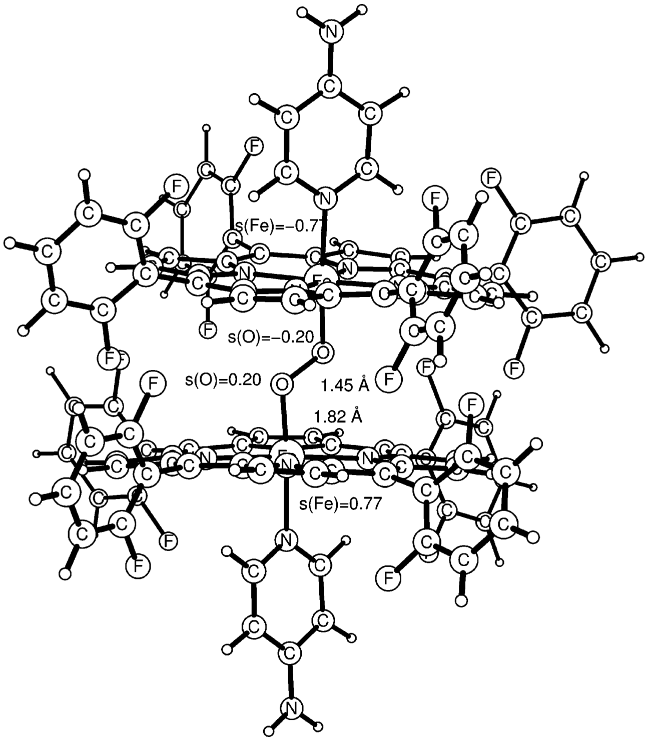

Figure 2. Optimized dinuclear iron peroxo complex with axial ligands. The most important interatomic distances and spin populations are given. The corresponding unsubstituted complex has the same structural parameters.

noted that the process of formation of the dinuclear peroxo complex is not considered here. There are too many difficulties involved in the modeling of this process, concerning, for example, the entropy loss and solvent effects when going from monomers to the peroxo dimer complexes. It can be mentioned, though, that in the gas phase both dinuclear F_8TPPFe peroxo complexes (with and without axial ligands) are strongly bound relative to two F_8TPPFe^{II} monomers and free molecular oxygen at the B3LYP level. Using the present types of methods, it is not possible to estimate the solvent effects when going from the monomers to the dimer complexes.

The O−O bond cleavage reaction was investigated for several different singlet (antiferromagnetic coupling) states of the dinuclear peroxo complexes. For the singlet state formed from low-spin iron ions ($S = \pm^1/_2$), transition states were optimized for all four systems, i.e., with and without the substituents on the porphyrin and with and without the axial base. The resulting structural parameters and spin populations characterizing each transition state are given in Table 3. The electronic activation energies on the potential energy surface of the low-spin iron state ($S = \pm^1/_2$) are also given in the table. As noted in the previous section, this low-spin iron state is sometimes not the ground state of the reactant peroxo state, which means that in some cases the activation barrier is higher than the intrinsic barriers shown in Table 3, as will be discussed in the next section. One main conclusion that can be drawn from the results in Table 3 is that the substituents on the porphyrin ring have very small effects on the O−O bond cleavage reaction. Concerning the effect of the axial base, the activation energy on the low-spin ($S = \pm^1/_2$) surface is about 14 kcal/mol without and about 21 kcal/mol with this base for both the Porf and F_8TPP ligands. The use of B3LYP* has a rather small effect on the barrier heights, decreasing them to about 12 and 20 kcal/mol, respectively. A second conclusion is that the presence of the axial ligands appears to raise the barrier on the low-spin ($S = \pm^1/_2$) surface by 6−8 kcal/mol. This can also be described as a decrease of the binding energy between the axial ligand and iron when going from the reactant to the transition state. Actually, the calculations indicate that the binding energy of each axial ligand decreases from 19.3 kcal/mol in the peroxo reactant to 15.5 kcal/mol in the ferryl (Fe^{IV}=O) product, i.e., a total decrease by 2 × 3.8 = 7.6 kcal/mol during the O−O bond cleavage reaction. This means that the entire effect of the decreased axial ligand binding energy during the reaction occurs already at the transition state. As can also be seen from Table 3, the transition state is somewhat later when the axial ligands are present; the O−O bond distance in the transition state increases from 1.85 Å without the base to 2.00 Å with the base in the F_8TPP case. This is a natural consequence of the destabilizing effect on the axial ligand binding energy, raising later parts of the energy surface.

Table 3. Most Important Structural Parameters and Spin Populations for the O−O Bond Cleavage Transition States[a]

Fe ligand	axial ligand	R(O−O) (Å)	R(Fe−O) (Å)	spin Fe[b]	spin O[b]	$\Delta E^‡$ (kcal/mol)
Porf		1.90	1.69	0.94	0.76	14.2 (11.4)
Porf	DHAP	2.01	1.71	0.88	0.95	21.4 (18.9)
F_8TPP		1.85	1.72	0.92	0.67	14.0 (12.1)
F_8TPP	DHAP	2.00	1.73	0.86	0.93	20.5 (20.1)

[a] Relative energy on the low-spin ($S = \pm^1/_2$) energy surface. B3LYP* values are given in parentheses. [b] On one unit; the other one has the same values with opposite sign.

Calculations were also performed on the singlet states composed from antiferromagnetic coupling of intermediate-spin ($S = \pm^3/_2$) and high-spin ($S = \pm^5/_2$) iron ions. In all cases, the energy increases significantly when the O−O bond distance is increased, such that the low-spin ($S = \pm^1/_2$) transition states described in the previous paragraph are always lowest in energy for the O−O bond cleavage reaction.

IIIc. Comparison to Experimental Results. Karlin et al.[2] found that, in a noncoordinating solvent at $T = 193$ K, F_8TPPFe^{II} forms stable dinuclear peroxo complexes, as shown in Figure 1. Furthermore, if the strong base DMAP is added after the peroxo complexes are formed, the O−O bond is immediately cleaved at the same temperature and Fe^{IV}=O complexes are observed. To compare the calculated results to the experimental observations, free-energy activation barriers have to be calculated. This means that the barriers reported in Table 3 have to be related to the corresponding ground states of the peroxo compounds; see Table 2. The resulting activation energies, including also zero-point and thermal effects at $T = 193$ K, both $\Delta H^‡$ and $\Delta G^‡$, are reported in Table 4.

For the situation without a base present, the results in Table 4 agree very well with experiment in the sense that the calculated free-energy barrier of 33.7 kcal/mol prevents any

Table 4. Calculated Activation Parameters for the O−O Bond Cleavage Relative to the Respective Reactant Ground State for Each Dinuclear Peroxo Complex at $T = 193$ K[a]

Fe ligand	axial ligand	**Δ$H^\ddagger$ (kcal/mol)**	**Δ$G^\ddagger$ (kcal/mol)**
Porf		29.2 (17.3)	31.4 (19.5)
Porf	DHAP	19.7 (17.2)	20.3 (17.8)
F_8TPP		31.5 (20.3)	33.7 (22.5)
F_8TPP	DHAP	18.8 (18.4)	19.4 (19.0)

[a] B3LYP* values are given in parentheses.

O−O bond cleavage. However, a large part of the barrier comes from the splitting between the high-spin ($S = \pm^5/_2$) and low-spin ($S = \pm^1/_2$) states for the reactant, and as shown in Table 2, this splitting is very sensitive to the amount of Hartree−Fock exchange and, therefore, rather uncertain. Still, the $\Delta G^\ddagger$ value calculated using B3LYP*, 22.5 kcal/mol, also prevents the O−O bond cleavage on a reasonable time scale at $T = 193$ K. It could, of course, be argued that with even less Hartree−Fock exchange, e.g., at the BLYP level, even the order of the states might change, such that the low-spin ($S = \pm^1/_2$) state actually becomes the ground state. However, results to be discussed below implies that the high spin ($S = \pm^5/_2$) is actually the ground state for the peroxo complex, in accordance with the B3LYP and B3LYP* results. When the base is added, the O−O bond cleavage is experimentally observed to occur rather fast. No rate was given, but the free-energy barrier should probably not be higher than 13 kcal/mol, corresponding to a rate of 1 reaction per minute at $T = 193$ K. The calculations indicate two different opposing effects on the barrier height from the addition of the base. First, the ground state of the reactant is changed from the high-spin ($S = \pm^5/_2$) state to the low-spin ($S = \pm^1/_2$) state, as discussed above, and therefore the barrier is decreased. This effect is most likely the reason why the reaction can occur on a reasonable time scale when the base is added. On the other hand, as is also discussed above, the addition of the axial ligand increases the intrinsic barrier on the low-spin ($S = \pm^1/_2$) surface because of the decreased binding of the axial ligand during the reaction. The calculations give a very large effect for this, raising the barrier by 7−8 kcal/mol, yielding a $\Delta G^\ddagger$ value as high as 19.4 kcal/mol. It is clear that this value is too high to explain the experimental observations of a fast O−O bond cleavage reaction at $T = 193$ K. The error of at least 6 kcal/mol is somewhat larger than what is typical for this kind of reaction. The error is mainly due to the incorrect dissociation of the O−O bond by a single determinant, but it is likely that part of the error in the calculated barrier involves the description of the variation of the axial ligand binding energy. A better chemical model involving the explicit description of the solvent interaction might be needed to improve the results.

The present results can also be compared to previous experimental results for similar porphyrin complexes. Balch et al. were the first to observe these types of dinuclear peroxo complexes, using *meso*-tetrakis(*m*-tolylporphyrin)iron(II) (TmTPFe).[3] They did experiments on a series of different porphyrins, and as the results from the present investigation show, the substituents on the porphyrin rings do not seem to significantly affect either the state splittings or the O−O bond cleavage barriers. Therefore, the present results can be compared also to the results by Balch and co-workers. In particular, for the TmTP ligand, an indefinitely stable dinuclear complex was observed in a noncoordinating solvent at $T = 203$ K, and when the temperature was increased, a reaction that was interpreted as an O−O bond cleavage occurred. From the temperature dependence, kinetic parameters could be determined, and $\Delta H^\ddagger$ was found to be 14.5 kcal/mol and $\Delta S^\ddagger$ 15 cal/K·mol.[4] Thus, from experiment, there is a clear entropy effect on the activation energy, corresponding to an increase of 3.0 kcal/mol at $T = 193$ K. This effect is well represented by the calculations with 2.2 kcal/mol; see Table 4 (no axial ligand). It is interesting to note that this entropy effect on the barrier height is a result of the switching of spin surfaces, from the high-spin ($S = \pm^5/_2$) state for the reactant to the low-spin ($S = \pm^1/_2$) state at the transition state. If the kinetic parameters for the complex without axial ligands are calculated relative to the low-spin ($S = \pm^1/_2$) reactant, the entropy effect actually decreases the barrier slightly (0.6 kcal/mol). Also, as can be seen in Table 4 for the system with the axial ligands present and where no spin switch occurs, there is only a very small entropy effect. Therefore, it is concluded that for the complex without axial ligands the ground state for the peroxo complex is actually high spin ($S = \pm^5/_2$), as the present calculations indicate, leading to a spin switch during the O−O bond cleavage reaction.

The calculated $\Delta H^\ddagger$ value of 31.5 kcal/mol for the F_8TPP complex with no axial ligand is much too high compared to the experimental value of 14.5 kcal/mol. However, as discussed above, the calculated value contains the uncertain spin splitting of the reactant, and using the B3LYP* value of 20.3 kcal/mol for $\Delta H^\ddagger$ gives a much better agreement with experiment, even if it is still somewhat worse than what is typical for this kind of O−O bond cleavage reaction. As was also discussed above, the main reason for the unusually large uncertainty in this activation barrier is that it involves a change of the spin state between the reactant and the transition state and that the spin is changed in two steps for two metal centers, resulting in an error that tends to be 4 times larger than usual.

IV. Conclusions

The main purpose of the present study is to explain the experimental result that a dinuclear porphyrin peroxo complex that is indefinitely stable at low temperature in a noncoordinating solvent dissociates into two ferryl−oxo complexes when a strong base is added.[2] The calculations show that an important effect of the base, which forms a strong axial ligand to each iron in the peroxo complex, is to change the ground state of the complex. For the peroxo complex without axial ligands, the antiferromagnetic coupling of two high-spin irons ($S = \pm^5/_2$) is the ground state, while the presence of the axial ligands makes the antiferromagnetic coupling of two low-spin irons ($S = \pm^1/_2$) the ground state. Because in the O−O bond cleavage transition state region the low-spin ($S = \pm^1/_2$) state is the lowest one in both cases, this means that without axial ligands the complex first has to be promoted to the reacting surface, making the barrier higher than that in the other case with axial ligands present. General aspects of spin-crossings during chemical reactions are discussed in ref 22.

A complicating factor in the interpretation of the computational results is the fact that the energy splitting between the different spin states in the dimer peroxo complex is unusually difficult to determine accurately. The reason is that, apart from the fact that there are two metal centers involved, on each atom there are two steps of spin recoupling between the ground state ($S = \pm^5/_2$) and the reacting state ($S = \pm^1/_2$). This makes the computed splitting, which directly enters the O−O bond cleavage barrier when no base is present, extremely sensitive to the amount of exact exchange in the functional used. On the other hand, the computed entropy effect supports the conclusion on the spin state switch. The experimentally determined entropy effect on the activation energy[4] can only be reproduced if a state switch is implied for the O−O bond cleavage reaction. When it comes to the value for the splitting, it turns out that the use of the modified functional B3LYP* yields a reasonable agreement with experiments by Balch et al. for the activation parameters for similar porphyrin complexes[4] without a base. The computed activation enthalpy at the B3LYP* level is 6 kcal/mol too high, which is almost within normal error bounds. Part of this error is likely to be in the intrinsic barrier on the low-spin surface, typical for bond cleavage reactions, and part in the splitting between the states.

Another complicating factor is the fact that the axial ligands, i.e., the addition of the base, appear to increase the intrinsic barrier on the low-spin ($S = \pm^1/_2$) surface, thus opposing the effect of the switch of the ground state. It also seems as if the error in the calculated activation energy with the axial ligands present is larger than 6 kcal/mol, although there is no state switch involved. It therefore seems as if in this case there is an additional error involved, which comes from the description of the change in the axial ligand binding during the O−O bond cleavage reaction. Possibly, this error originates from the chemical model used, rather than from the DFT functional.

Supporting Information Available: Cartesian coordinates for optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC7007182

---

(22) Harvey, J. N. *Phys. Chem. Chem. Phys.* **2007**, *9*, 331−343.