

Abstraction of the Hydrogen Atom of Methane by Iron–Oxo Species: The Concerted Reaction Path Is Energetically More Favorable

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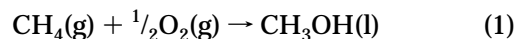
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Two kinds of H-atom abstractions from methane by iron–oxo complexes with different charges are discussed from density functional theory calculations. A concerted H-atom abstraction via a four-centered transition state is shown to be energetically more favorable than a direct H-atom abstraction via a transition state with a linear C–H–O array. Iron(IV)–oxo complexes appear to be the most effective for the cleavage of the C–H bond of alkanes in the concerted mechanism, which is rationalized from qualitative orbital interaction analyses. The results of this paper support the establishment of the two-step concerted mechanism that we have proposed for alkane hydroxylations by iron–oxo species. The proposed reaction mechanism may have relevance to our understanding of some catalytic and enzymatic processes concerning alkane hydroxylations if coordinatively unsaturated transition-metal oxides are responsible for such important chemical reactions.

Introduction

Activation of methane and small alkanes^{1–9} is currently an important subject in pure and applied chemistry. Considering the recent demand for methanol as a fuel and a starting material for many industrial processes, new chemical processes must be developed for efficient production of methanol. The industrial process available for the production of methanol from natural gas, which mainly consists of methane, involves two-step reactions via the formation of synthesis gas, i.e., carbon monoxide and dihydrogen.^{5,6}

Direct conversion of methane to methanol (indicated in eq 1), which actually occurs in enzymatic^{10,11} and gas-phase reactions,^{12,13} is thermodynamically more efficient than the commercial two-step process via synthesis gas.



$$\Delta H^\circ = -30.7 \text{ kcal/mol}$$

Hydrogen-atom abstraction occurring in the initial stages of the reaction is the key to understanding such direct hydrocarbon hydroxylations. The active species of compound **I** of cytochrome P450¹¹ and intermediate **Q** of methane monooxygenase (MMO)¹⁴ are proposed to

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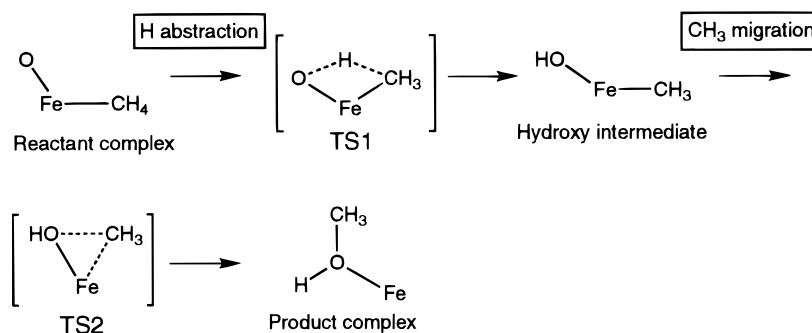
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Scheme 1



involve one or two ferryl moieties, Fe(IV)=O . The hydroxylation by P450 has been considered to occur by a radical mechanism involving a direct H-atom abstraction from the substrate, followed by a rapid transfer of a metal-bound hydroxy radical to an intermediate alkyl radical.¹¹ Such a widely believed radical mechanism is called an “oxygen rebound mechanism”.

The gas-phase C–H bond activation of small hydrocarbons (by various transition-metal–oxide ions and bare metal cations) has been experimentally investigated in Schwarz’s¹² and Armentrout’s¹³ laboratories. The gas-phase methane–methanol conversion by metal–oxide ions is of particular interest since this process may be viewed as the simplest model for alkane hydroxylation. On the basis of observed isotope effects, Schröder and Schwarz^{12a} have suggested that a reaction species, $\text{HO–Fe}^+ \text{---} \text{CH}_3$, is the central intermediate in the reaction between FeO^+ and CH_4 . Armentrout et al.^{13j} have investigated the mechanism and energetics involved in the gas-phase methane–methanol conversion by CoO^+ and its reverse reaction.

Activation of the C–H bonds of methane by transition-metal complexes has been theoretically studied by many research groups.^{15–21} In a recent paper,²² we proposed a favorable reaction pathway for the direct

methane–methanol conversion by the bare FeO^+ complex on the basis of Fukui’s IRC (intrinsic reaction coordinate) analysis.²³ From our recent studies,^{22,24} new findings can be derived on the reaction pathway for the conversion of methane to methanol: (1) a C_{3v} or D_{2d} distorted methane can be activated on a coordinatively unsaturated iron–oxo species, leading to the formation of a reactant complex with Fe–C as well as Fe–H bonds, and (2) the conversion of methane to methanol should occur at an iron-active center through two-step concerted hydrogen and methyl migrations, as indicated in Scheme 1.

How H-atom abstraction occurs is, thus, of fundamental interest and the subject of an ongoing controversy in the literature. In this paper, the energetics of the two kinds of H-atom abstractions by bare FeO^{n+} complexes with different charges are compared from reliable DFT calculations, in which $n = 2, 1,$ and 0 . We show that the concerted reaction pathway via TS1 in Scheme 1 is energetically more favorable than the direct H-atom abstraction by the oxo species. We also suggest that such a concerted H-atom abstraction should proceed most efficiently on an iron(IV)–oxo species. The reader may think that gas-phase reactions are essentially different from complicated catalytic and enzymatic reactions. However, catalytically active metal centers are usually unsaturated in their coordination spheres so that the mechanism for the gas-phase reaction is not so unrealistic for catalytic alkane hydroxylations. In fact, we recently demonstrated from density functional theory (DFT) calculations that a dinuclear iron model complex of intermediate **Q** of MMO, in which the two iron centers are four- and five-coordinate, exhibits a similar four-centered transition state for a concerted H-atom abstraction.²⁵ We hope that the reader accepts our proposal as one of the possible mechanisms for H-atom abstraction.

Method of Calculation

We optimized local minima (on a potential energy hypersurface) corresponding to the reactant complexes, $\text{OFe}^{n+}(\text{CH}_4)$, and reaction intermediates, $\text{HO–Fe}^{n+} \text{---} \text{CH}_3$, using the hybrid

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(Hartree–Fock/density functional theory) B3LYP method. It consists of the Slater exchange, the Hartree–Fock exchange, the exchange functional of Becke,²⁶ the correlation functional of Lee, Yang, and Parr (LYP),²⁷ and the correlation functional of Vosco, Wilk, and Nusair.²⁸ The contribution of each energy to the B3LYP energy expression was fitted²⁶ empirically on a reference set of molecules. For the Fe atom, we used the (14s9p5d) primitive set of Wachters²⁹ supplemented with one polarization f-function ($\alpha = 1.05$),³⁰ resulting in a (611111111|51111|311|1) [9s5p3d1f] contraction, and for the H, C, and O atoms, we used the 6-311G** basis set of Pople and co-workers.³¹ These are referred to below as 6-311G** following the basis set code of the Gaussian 94 ab initio program package.³² Transition-state (TS) structures were also optimized at the same level of theory. Vibrational frequencies were systematically computed in order to ensure that on a potential energy surface all optimized geometries correspond to a local minimum that has no imaginary frequency or a saddle point that has only one imaginary frequency. Zero-point energy corrections were taken into account in calculating the total energies of the reactant complexes, intermediates, product complexes, and transition states. We performed orbital interaction analyses based on the extended Hückel method³³ with YAeHMOP.³⁴

Concerted H-Atom Abstraction by Iron–Oxo Species

We compare the reactivities of FeO^{2+} , FeO^+ , and FeO toward methane. In these species, only FeO^+ is available for chemical reactions under ion-cyclotron-resonance conditions,^{12,13} and FeO^+ was discovered by Schröder and Schwarz^{12a} to convert methane to methanol in the gas phase. It is interesting to know how different the reactivity of FeO^+ is from that of dicationic FeO^{2+} and neutral FeO so that theoretical analyses of the reactivities of FeO^{2+} and FeO toward methane and small alkanes are worthy of performing. Thermodynamic data for these two species have been derived from various mass-spectrometric measurements and ab initio calculations.³⁵ The model FeO^{2+} and FeO species are, of course, isoelectronic, respectively, to MnO^+ and CoO^+ , the reactivities of which have been studied in detail.^{12i,13j} We took a quintet state for FeO^{2+} , quartet and sextet states for FeO^+ , and triplet and quartet states for FeO into account following our previous papers.²²

The potential energy diagrams for the concerted reaction pathways for the H-atom abstraction from

methane by FeO^{2+} , FeO^+ , and FeO , occurring via TS1, are shown in Figure 1. Interestingly, the activation energy of 4.9 kcal/mol for the H-atom abstraction by the FeO^{2+} species is much smaller than that in the FeO^+ and FeO cases. This value is comparable to 9.4 kcal/mol in the isoelectronic MnO^+ case.^{22b} Although we have not included important ligand effects which often play an essential role in the reactivities of transition-metal complexes, this result may be useful in considering the reason iron(IV)–oxo species play a special role in C–H activations in the biological systems.^{10,11}

In Figure 1, we see interesting crossings between two potential energy surfaces of different spin states in the FeO^+ and FeO cases as the reaction goes from the reactant complex toward TS1. “Two-state reactivity” has been proposed by Shaik et al.^{12h,36} to play an important role in the activation of dihydrogen and alkanes by FeO^+ . The computed activation energy in the FeO^+ case is 31.1 and 15.7 kcal/mol in the sextet and quartet states, respectively; however, if we consider the surface crossing, it would reasonably be 22.1 kcal/mol. Also, in the neutral FeO case, the activation energy is 50.5 and 12.0 kcal/mol in the quintet and triplet states, respectively, and it would be 22.0 kcal/mol taking the spin inversion into account. In contrast to FeO^+ and FeO , the spin inversion is unlikely to play a role in the FeO^{2+} case. Only the quintet state plays a role in the C–H activation by FeO^{2+} , which is again consistent with the isoelectronic MnO^+ case.^{12i,22b}

Figure 2 shows the essential structural features of the minima and transition states for the quintet state for the FeO^{2+} case, the sextet state for the FeO^+ case, and the quintet state for the FeO case. Let us first look at the reactant complexes. These initially formed species exhibit an η^3 - or η^2 -binding mode; it is difficult to afford a good reason that an η^3 -binding mode is adopted in the $\text{OFe}^{2+}(\text{CH}_4)$ complex and another mode in the $\text{OFe}^+(\text{CH}_4)$ and $\text{OFe}(\text{CH}_4)$ complexes, because these two modes are close-lying in energy. Morokuma and Koga and their collaborators¹⁹ have studied this subject in detail for different metal complexes, but to the best of our knowledge, a clear-cut answer has not yet been afforded. A computed binding energy of 70 kcal/mol for the formation of the $\text{OFe}^{2+}(\text{CH}_4)$ complex is extremely large compared with those in the FeO^+ and FeO cases because FeO^{2+} behaves as an electron acceptor, leading to the formation of a strongly bound reactant complex. Thus, the total charge of the methane in $\text{OFe}^{2+}(\text{CH}_4)$ was calculated to be +0.41, while that in $\text{OFe}^+(\text{CH}_4)$ is +0.12, and that in $\text{OFe}(\text{CH}_4)$ is –0.07. As a consequence, a calculated Fe–C distance of 2.07 Å in the quintet state of $\text{OFe}^{2+}(\text{CH}_4)$ is 0.3 Å shorter than those in $\text{OFe}^+(\text{CH}_4)$ and 0.25 Å shorter than those in $\text{OFe}(\text{CH}_4)$, as shown in Figure 2, although the binding modes are different. We think that the particularly strong bond between CH_4 and FeO^{2+} is due to the participation of a vacant $3d\sigma$ orbital to the bonding. The large binding energy of 70 kcal/mol in the $\text{OFe}^{2+}(\text{CH}_4)$ complex would have no relevance to catalytic and enzymatic reactions because they do not take place on such highly charged transition-metal complexes. It is probably important to state that the binding energy in the

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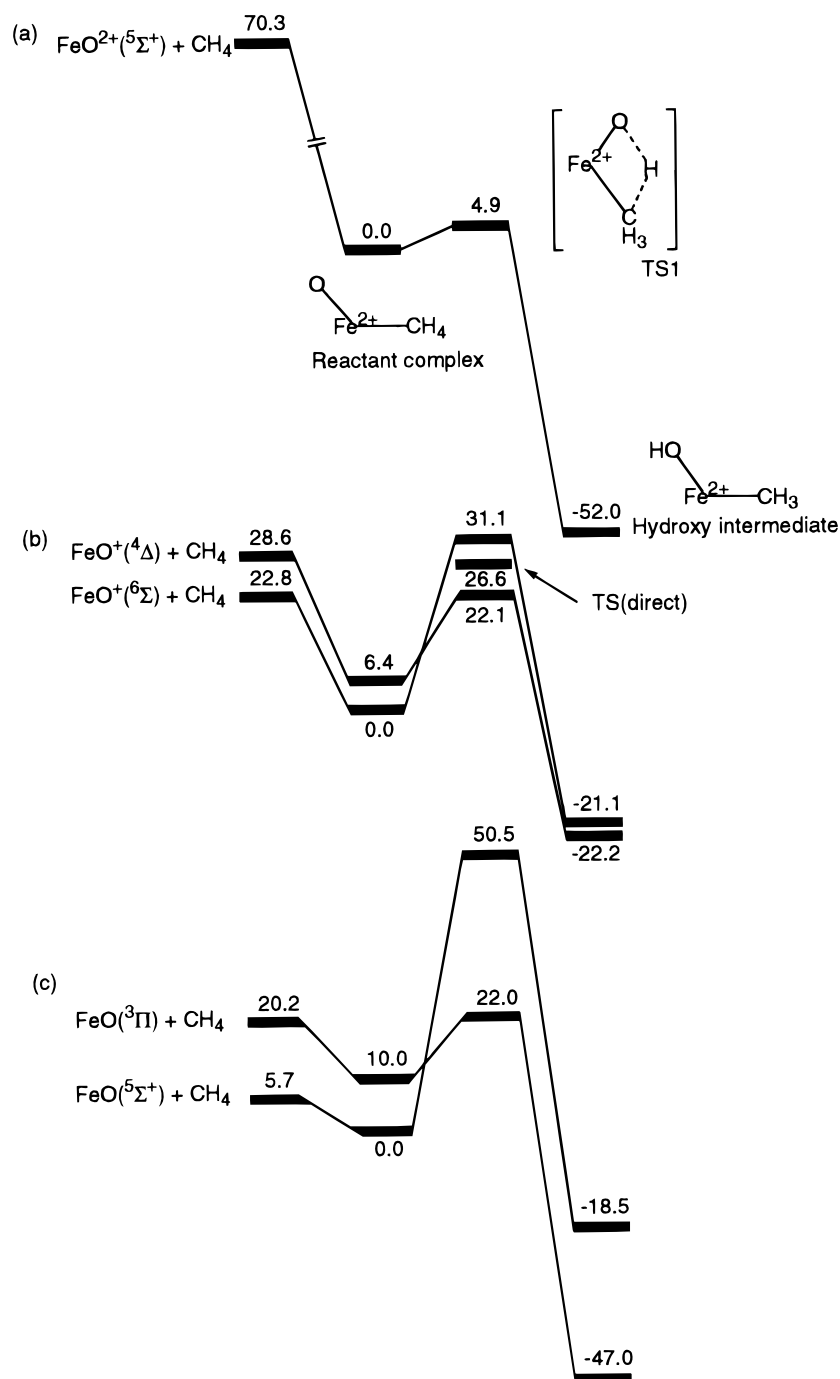


Figure 1. Potential energy diagrams along concerted H-atom abstraction pathways. Relative energies are in kcal/mol. TS(direct) is a transition state along a direct H-atom abstraction pathway in the sextet state.

isoelectronic $\text{OMn}^+(\text{CH}_4)$ complex is computed to be 16 kcal/mol at the same level of theory.^{22b}

The methane in the $\text{OFe}^{2+}(\text{CH}_4)$ complex is, thus, significantly activated, and the C–H bonds should be weakened a great deal because of the electron transfer occurring mainly from the HOMO of methane, which is composed of C–H bonding orbitals.^{24b} The reader may, therefore, think that the computed low activation energy for the H-atom abstraction in the dicationic case should be ascribed mainly to the significant charge transfer in the reactant complex, but this view is not necessarily correct as orbital interaction analyses for TS1 will demonstrate in the following section. In fact, isoelectronic MnO^+ also affords a small activation energy of 9.4 kcal/mol at the same level of theory,^{22b}

while the total charge of the methane in the $\text{OMn}^+(\text{CH}_4)$ complex is calculated to be +0.11. We, therefore, think that there is another important factor that should govern the C–H bond dissociation of methane and small alkanes.

In the neutral FeO case, the nature of the $\text{OFe}(\text{CH}_4)$ complex differs from that of the $\text{OFe}^{2+}(\text{CH}_4)$ and $\text{OFe}^+(\text{CH}_4)$ complexes, which can be viewed as ion-induced dipole complexes, and thus, the binding energy in the $\text{OFe}(\text{CH}_4)$ complex (5.7 kcal/mol in the quintet ground state) is small compared with that in the $\text{OFe}^{2+}(\text{CH}_4)$ and $\text{OFe}^+(\text{CH}_4)$ complexes. As a consequence, we expect that FeO exhibits little reactivity toward methane because the formation of the reactant complex, which

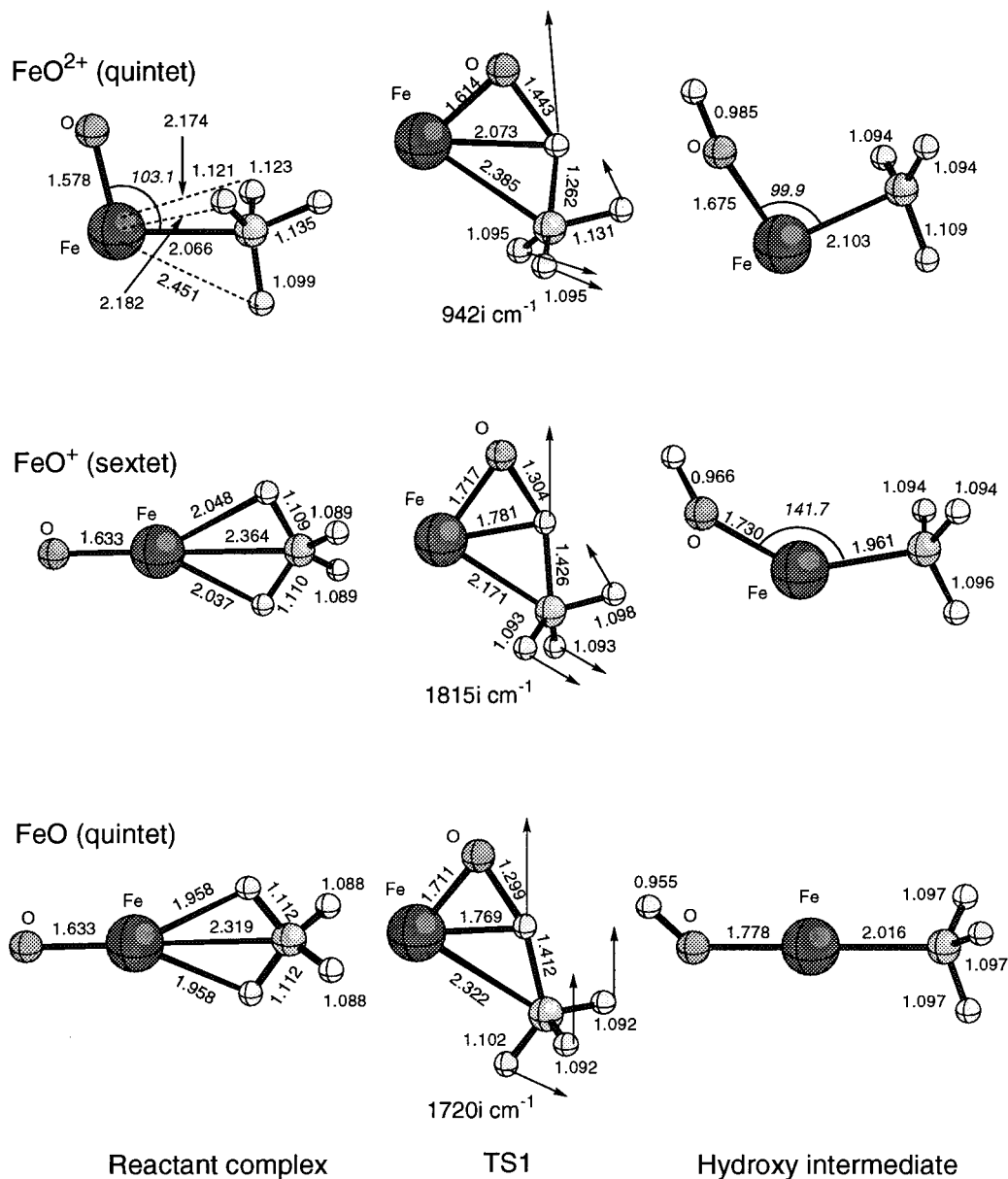


Figure 2. Optimized geometries of the reactant complexes, TS1s, and the hydroxy intermediates in the quintet state of the FeO^{2+} case, the sextet state of the FeO^+ case, and the quintet state of the FeO case.

we believe to be an essential process for methane activation, is unlikely to occur in the neutral FeO case.

The concerted H-atom abstraction occurs in each case, via four-centered TS1, to lead to the hydroxy intermediate, $\text{HO-Fe}^{n+}-\text{CH}_3$. The structures of TS1 in the different charge states, indicated in Figure 2, are quite similar each other, and the transition vectors ensure that this transition state correctly connects the reactant complex and the hydroxy intermediate. In a previous paper,^{22a} we confirmed this point from detailed IRC analyses. The geometries of the hydroxy intermediate are a little different in the different charge and spin states, especially for the bending angle of the C–Fe–O moiety.

Since the FeO^{2+} dication is metastable, due to repulsive Coulombic interactions, and it is potentially dissociated into Fe^+ and O^+ ,³⁵ it may be useful to consider a dissociation into the CH_3^+ and FeOH^+ fragments. As mentioned below, a direct H-atom abstraction is unlikely to occur in this charge state, so that such a

dissociation is expected to occur after the formation of the hydroxy intermediate, which is easily generated as shown in Figure 1. We predict that this fragmentation will reasonably occur from an energetic point of view since it is about 70 kcal/mol more stable than the hydroxy intermediate. The electrostatic repulsion in the dicationic species is a principal reason for such a fragmentation into the two monocationic species. Another important fragmentation is that into Fe^+ and $\text{CH}_3\text{-OH}^+$, which are generated via TS2 and the product complex as indicated in Scheme 1. The two fragmentation reactions are energetically competitive, the former one lying 5.7 kcal/mol below the latter one. In addition to these fragmentations, we were very interested in the other fragmentations into Fe^{2+} and neutral CH_3OH , which can also be generated after the formation of the product complex, but this reaction is energetically unfavorable. The energetics for interesting chemical species generated from the reaction between FeO^{2+} and methane is shown in Figure 3. The reaction of FeO^{2+}

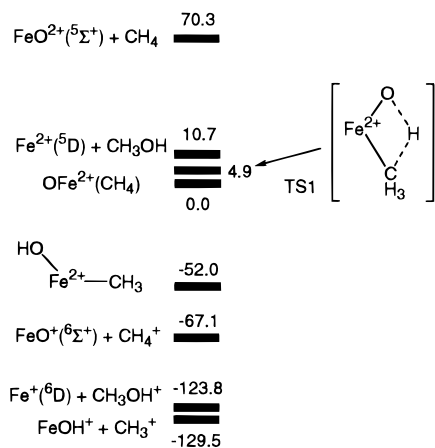


Figure 3. Energetics for chemical species in the reaction of FeO^{2+} with methane. Values are in kcal/mol.

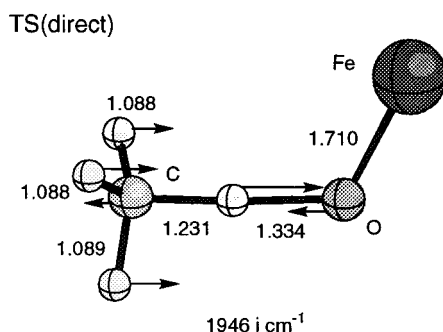


Figure 4. Transition-state structure for a direct H-atom abstraction pathway in the sextet state of the FeO^+ case. Transition vectors and imaginary frequency are indicated.

with methane is, thus, quite interesting and fruitful, so we decided to determine the experimentally observed branching ratio of these interesting reaction species if such experimental conditions were available.

Direct H-Atom Abstraction by Iron–Oxo Species

Let us next look at the direct H-atom abstraction (by the oxo species), which is widely believed to play a role in C–H bond dissociations by various transition-metal complexes, especially in biological oxidation of hydrocarbons.¹¹ We found that a direct H-atom abstraction occurs only in the sextet state of the FeO^+ case. This fact will be verified from orbital interaction analyses in the next section. The geometry of the transition states along the direct abstraction pathway, TS(direct), is shown in Figure 4; TS(direct) exhibits a nearly linear C–H–O array, as expected from a conventional radical mechanism. The geometry is, of course, similar to the essential part of the corresponding transition states of model complexes of P450 and MMO calculated by Siegbahn and Crabtree.³⁷ The transition vectors indicated in Figure 4 clearly tell us that this transition state is responsible for a dissociation into FeOH and CH_3 fragments and does not lead to the formation of the important hydroxy intermediate, $\text{HO–Fe}^+–\text{CH}_3$. We, therefore, do not think that TS(direct) will result in the hydroxylation of methane along a simple reaction

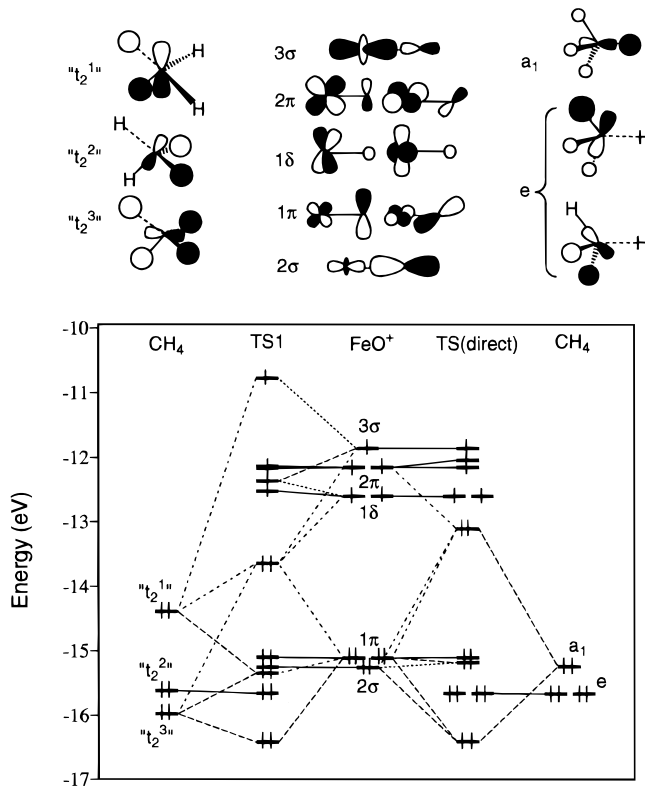


Figure 5. Fragment molecular orbital (FMO) analyses for TS1 and TS(direct) in the sextet state of FeO^+ .

pathway. As shown in Figure 1, TS(direct) appeared to lie 4.5 kcal/mol above the concerted TS1 in the quartet state of the FeO^+ case. We can, therefore, conclude from an energetic viewpoint that such a direct H-atom abstraction is unlikely to occur, at least in the gas-phase methane activation by iron–oxo species with different charges.

Fragment Molecular Orbital Analyses

To have a better understanding of the two kinds of H-atom abstractions discussed above from DFT calculations, it is very useful to look in detail at fragment molecular orbital (FMO) analyses. We do not need to know the details of the electronic structures of the fragments; it is sufficient that we look at the frontier orbitals of the fragments and their reconstructions. The theoretical background of the FMO method lies in perturbation molecular orbital theory.³⁸ Let us now consider why FeO^{2+} and MnO^+ , which can be formally viewed as d^4 complexes, activate methane C–H bonds more efficiently than any other species. The orbital interactions in TS1 and TS(direct), which are theoretically partitioned into the FeO and CH_4 fragments, are shown in Figure 5. The sextet-state geometries in the FeO^+ case, shown in Figures 2 and 4, were adopted for the extended Hückel calculations. The spin states indicated in the illustrations in Figure 5 are sextet.

The molecular orbitals of the FeO fragment are indicated at the center in Figure 5. The 2σ and 1π orbitals are localized mainly on the oxygen, but the 1δ ,

(37) Siegbahn, P. E. M.; Crabtree, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3103.

(38) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

2π , and 3σ orbitals are localized more on the iron; the 1δ , 2π , and 3σ orbitals can, thus, be viewed as d-block orbitals. The orbital interactions for TS1 and TS(direct) are indicated to the left and right, respectively. In TS1, the 3σ orbital in the FeO fragment is significantly pushed up to -10.5 eV due to an interaction with the “ t_2 ” HOMO of the CH_4 fragment, so that the sextet state of TS1 in the FeO^+ case is energetically unstable within the framework of one-electron theory. In contrast to the sextet state, TS1 in the low-spin quartet state can be stabilized in the FeO^+ case because the destabilized orbital at -10.5 eV is not filled in the quartet state. On the other hand, TS1 should be greatly stabilized in the quintet state of the FeO^{2+} case because the destabilized 3σ orbital is unfilled in this state and exchange interactions among the four electrons housed in the four low-lying d-block orbitals can work reasonably well to stabilize the quintet state. We can, thus, conclude that the concerted H-atom abstraction is governed by the orbital energies and the number of electrons concerned with TS1. One can conclude that the FeO^{2+} case should be preferred the most for TS1 from an energetic viewpoint. In this way, we can rationalize why methane and small alkanes are efficiently activated by isoelectronic FeO^{2+} and MnO^+ . The low activation barriers for the C–H bond dissociation by these d^4 species are not due to a charge effect, in contrast to the binding energies in the $\text{OFe}^{2+}(\text{CH}_4)$ and $\text{OMn}^+(\text{CH}_4)$ complexes.

Next, let us find a good reason that direct H-atom abstraction is computed to exist only in the sextet state of FeO^+ . As shown in the FMO analysis for TS(direct) at the right in Figure 5, the a_1 HOMO of the CH_4 fragment interacts with the 2σ and 1π orbitals of the FeO fragment that are localized mainly on the oxygen. The electronic structure of TS(direct) is expected to be greatly stabilized in the sextet state of the FeO^+ case because all of the d-block orbitals lying within a range from -12.6 to -11.8 eV are singly occupied, and consequently, exchange interactions can work well among the five electrons with the same spin housed in the close-lying five d-block orbitals. If one electron is removed from one of the orbitals as in the FeO^{2+} case, we believe that the electronic structure of TS(direct) should be destabilized because there are four electrons in the close-lying five d-block orbitals. Thus, we could reasonably not find TS(direct) in the FeO^{2+} case from DFT calculations. Thus, qualitative FMO analyses for the transition states are useful for a better understanding of the reactivities of iron–oxo species in different charge and spin states.

Conclusions

Important two conclusions can be derived from this study. The first of these is that the concerted reaction

Table 1. Extended Hückel Parameters for Fe, O, C, and H Atoms

orbital	H_{ii} (eV)	ζ_{i1}	c_1	ζ_{i2}	c_2
Fe4s	-9.1	1.9			
Fe4p	-5.32	1.9			
Fe3d	-12.6	5.35	0.5505	2.00	0.6260
O2s	-32.3	2.275			
O2p	-14.8	2.275			
C2s	-21.4	1.625			
C2p	-11.4	1.625			
H1s	-13.6	1.3			

pathway, via a four-centered transition state (TS1 in Scheme 1), is energetically more favorable than the direct H-atom abstraction pathway, via a conventional transition state with a linear C–H–O array. Second, iron(IV)–oxo species are most effective for the cleavage of the C–H bond of alkanes in the concerted mechanism. We did not include important ligand effects which sometimes govern the reactivities of transition-metal complexes, but we believe that essential profiles in the catalytic and enzymatic reactions can be reasonably drawn from our mechanism if a coordinatively unsaturated iron–oxo species is responsible for such reactions. The results of this paper may lead to a rejection of the radical mechanism and to the establishment of the two-step concerted mechanism²² for alkane hydroxylations by various iron–oxo species.

In 1976, Joseph Chatt stated at an international conference, “I believe that in twenty-five years methane will be the most popular ligand in coordination chemistry”.³⁹ Our mechanism for methane C–H bond activation is consistent with his statement.

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Appendix

Extended Hückel calculations were carried out using YAeHMOP;³⁴ the parameters used for iron, oxygen, carbon, and hydrogen appear in Table 1.

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(39) Statement at the 17th International Conference on Coordination Chemistry, Hamburg, 1976; see also Chapter 2 of ref 1b.