Chemical Basis for High Activity in Oxygenation of Cyclohexane Catalyzed by Dinuclear Iron(III) Complexes with Ethereal Oxygen Containing Ligand and Hydrogen Peroxide System

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Ethereal Oxygen, Cyclohexane, Dinuclear Iron(III) Complexes

The crystal structures of two binuclear iron(III) complexes with linear μ-oxo bridge, Fe2OCl2(tfpy)2(C104)2·2CH3CN and Fe2OCl2(epy)2(C104)2 were determined, where (tfpy) and (epy) represent N,N-bis(2-pyridylmethyl)-2-ethoxyethylamine and N,N-bis(2-pyridylmethyl)-2-ethoxymethylamine, respectively. Their structural features are essentially the same as that of the corresponding linear binuclear complex with (tpa)-ligand, Fe2OCl2(tpa)2(C104)2, where (tpa) is tris(2-pyridylmethyl)amine: the ligands (tfpy) and (epy) act as a tetradentate tripod-like ligand, and Fe–O (ethereal oxygen atom; these are located at the trans-position of bridging oxo-oxygen atom) distances are 2.209(4) and 2.264(2) Å for (tfpy) and (epy) compounds, respectively. These two (tfpy) and (epy) complexes exhibited much higher activity for the oxygenation of cyclohexane in the presence of hydrogen peroxide than that of the (tpa) complex. In contrast to this, the former two complexes exhibit negligible activity for the decomposition of hydrogen peroxide, whereas the catalase-like function of the (tpa) compound is remarkable. These are indicating that an active species for oxygenation of cyclohexane, which is assumed to be an iron(III)-hydroperoxide adduct with η1-coordination mode, should be different from that is operating for decomposition of hydrogen peroxide; for the latter case formation of a (μ-η1:η1-peroxo)diiron(III) species being stressed. The EHMO calculation showed that electronic interaction between the monodentate hydroperoxide adduct of the binuclear iron(III)-(tfpy) compound and the tetrahydrofuran ring of the ligand system may lead to facile peroxide-tetrahydrofuran linkage formation, and the interaction described above should promote the O–O cleavage of the peroxide ion heterolytically. Based on these discussions, it was concluded that heterolytic O–O bond cleavage of the iron(III)-hydroperoxide adduct caused by electronic interaction with organic moiety containing an ethereal-oxygen and by approach of the substrate which donates electron to the peroxide adduct should play an important role in producing a high-valent iron-oxo species in these systems. In the case of (tpa) complex, formation of a hydroperoxide adduct linking with the ligand system seems to be unfavorable because of both the steric and electronic reasons.

Introduction

The selective oxidation and functionalization of alkanes under mild conditions is an exciting scientific and economic goal [1]. Although much of the research has focused on oxidations catalyzed by metalloporphyrins (putative cytochrome P-450 mimics), there is a growing interest in catalysis by other types of metal complexes. Notably, Que and co-workers have characterized some non-heme iron catalysts with tripodal tris(2-pyridylmethyl)amine (tpa) ligands, [Fe(tpa)X2]+, and have employed these complexes together with tert-butyl hydroperoxide to oxidize cyclohexane or adamantane in acetonitrile at room temperature [2]. However, these complexes are substantially poorer alkane functionalization catalyst in the presence of hydrogen peroxide [3].

Fontecave et al. [4] and Fish et al. [5] have observed that dinuclear oxo-bridged non-heme iron complexes with bipyridine or tetradentate ligand exhibit high activity for oxygenation of cyclohexane in the presence of hydrogen peroxide, and Fontecave et al. [4] proposed that a high-valent iron-oxo species derived from a metal-peroxide intermediate, must participate in the alkane functionalization, i.e.,

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R-H + LFeIV = O →
R* + LFeIV-OH → R-OH + LFeIII

however, in their opinions the origin for the formation of an iron(IV)-oxo species is unclear, and this mechanism has recently been questioned by Nishida et al., [6] Arends et al. [7] and Newcomb et al. [8] on the different points of views.

In the previous paper, we have reported [9] that linear μ-oxo binuclear iron(III) compounds, Fe2OCl2(L)2+ (L=(tfpy) or (epy)) exhibit high activity for oxygenation reaction of cyclohexane in the presence of hydrogen peroxide, whereas the activity of the corresponding (tpa) complex is negligible under the same experimental conditions, where (tfpy) and (epy) denote N,N-bis(2-pyridylmethyl)-2-aminomethyltetrahydrofurfurylamine, N,N-bis(2-pyridylmethyl)-2-ethoxyethyl-amine, respectively (see Fig. 1). In addition to these, we have observed that the complexes with (tfpy) and (epy) show negligible activity for the decomposition of hydrogen peroxide, while the catalase-like function of the corresponding (tpa) complex is remarkable. These are suggesting that there may be two different kinds of an active iron(III) compounds in the solution [10]; one is active for the oxygenation of cyclohexane, and another one, active for decomposition of hydrogen peroxide. As an active species for oxygenation of cyclohexane in the solution of (tfpy)-complex, we have assumed formation of an Adduct I [9], illustrated below, where hydroperoxide ion which is coordinating to an iron(III) ion, is also interacting with the tetrahydrofuran ring of the (tfpy) ligand:

In this article we will show the experimental details on the preparation, crystal structure determinations, catalytic activities for oxygenation of cyclohexane and decomposition of hydrogen peroxide by the iron(III) complexes with (tfpy) and (epy), and would like to discuss the origin for high ability toward oxygenation of cyclohexane by the (tfpy)-complex.

**Experimental Section**

**Materials**

The ligands, (tfpy) and (epy) were obtained according to the methods reported by Toftlund et al. [11]. By the use of a methanol solution of the ligand, ferric chloride hexahydrate, and sodium perchlorate, mononuclear iron(III) complexes, FeCl2(tfpy)ClO4 and FeCl2(epy)ClO4 were obtained as yellow powder. From the methanol-water (10:1, v:v) solution containing the mononuclear iron(III) complex and stoichiometric amount of triethylamine, the desired complexes, Fe2OCl2(tfpy)2(ClO4)2 and Fe2OCl2(epy)2(ClO4)2 were obtained as orange crystals.

The (tfpy)-complex: Fe2Cl6C24H24N6O11 (964.25)
Calcd C 42.35 H 4.39 N 8.72%,
Found C 42.20 H 4.39 N 8.68%.

(epy)-complex: Fe2Cl6C30H38N6O11 (912.18)
Calcd C 39.50 H 4.20 N 9.21%,
Found C 39.13 H 4.22 N 9.11%.

**Crystal structure determinations**

The (tfpy) and (epy) complexes were recrystallized from aqueous-acetonitrile and aqueous-methanol solution. Crystal data were listed in Table I. X-ray diffraction intensities were measured up to 2θ=55° using MoKα radiation on a Rigaku four-circle diffractometer AFC-5. Absorption was corrected by a numerical integration method. Structure analysis was carried out using CRYSTAN-GM software version 6.2 on a SUN PARK10 workstation at Keio University [12].

**Catalase-like function of complexes**

All reactions were performed at 20 °C in a 10 cm³ reactor containing a stirring bar under air. The flask containing an iron(III) complex (10 μmole) solution (5 cm³, acetonitrile) was closed with a rubber septum. Hydrogen peroxide solution (1 cm³, commercial 30% aqueous solution was diluted to 1 M solution by acetonitrile) was injected through the septum with a syringe. The reactor was connected to a graduated burette filled with water and dioxygen evolved was measured at ap-
propriate time by volumetry. The theoretical quantity of dioxygen molecule, which should be evolved under our experimental condition, is ca. 16 cm³, which was exemplified by the authentic experiment by the use of MnO₂ as a catalyst.

Oxygenation reaction of cyclohexane in the presence of iron(III) complex and hydrogen peroxide

In a typical run, an acetonitrile solution (20 ml) containing iron(III) complex (0.05 mmole) and cyclohexane (840 mg) was added to an acetonitrile solution (10 ml) containing hydrogen peroxide (1.13 g of commercial 30% aqueous solution), and was kept to stand for at room temperature, and the oxygenated products were determined by GC. Cyclopentanone was used as an internal standard.

Molecular orbital calculations

The MNDO/AM1 calculations were performed for tetrahydrofuran, pyridine, and methylethyl ether, and the positional parameters of the compounds were optimized by the use of the AM1 program [13]. MO calculations for Fe(NH₃)₄(L)(HO₂⁻) were performed by the use of EHMO method reported by Hoffmann et al., [14] where (L) are tetrahydrofuran, dimethylether, and pyridine. The parameters used for the iron(III) ion are the same as those used in the literature [15].

**Table I. Crystal data of the iron(III) compounds.**

<table>
<thead>
<tr>
<th></th>
<th>(tfpy)</th>
<th>(epy)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>Fe₂OCl₂(tfpy)₂(ClO₄)₂·2CH₃CN</td>
<td>Fe₂OCl₂(epy)₂(ClO₄)₂</td>
</tr>
<tr>
<td><strong>M</strong></td>
<td>912.18</td>
<td>912.18</td>
</tr>
<tr>
<td><strong>Crystal symmetry</strong></td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P₁</td>
<td>P₁</td>
</tr>
<tr>
<td><strong>a [Å]</strong></td>
<td>11.273(2)</td>
<td>9.381(1)</td>
</tr>
<tr>
<td><strong>b [Å]</strong></td>
<td>12.650(3)</td>
<td>11.383(2)</td>
</tr>
<tr>
<td><strong>c [Å]</strong></td>
<td>8.605(1)</td>
<td>9.147(2)</td>
</tr>
<tr>
<td><strong>α [°]</strong></td>
<td>92.79(2)</td>
<td>96.15(2)</td>
</tr>
<tr>
<td><strong>β [°]</strong></td>
<td>99.42(1)</td>
<td>104.58(1)</td>
</tr>
<tr>
<td><strong>γ [°]</strong></td>
<td>74.27(1)</td>
<td>83.75(1)</td>
</tr>
<tr>
<td><strong>V [Å³]</strong></td>
<td>1165.2(4)</td>
<td>936.4(2)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>D [gcm⁻³]</strong></td>
<td>1.491</td>
<td>1.618</td>
</tr>
<tr>
<td><strong>μ(Mo-Kα) [cm⁻¹]</strong></td>
<td>9.16</td>
<td>11.25</td>
</tr>
<tr>
<td><strong>Observed reflections</strong></td>
<td>3486</td>
<td>3193</td>
</tr>
<tr>
<td><strong>(Fo&gt;3σ(Fo))</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>No. variables</strong></td>
<td>319</td>
<td>320</td>
</tr>
<tr>
<td><strong>R</strong></td>
<td>0.0704</td>
<td>0.0456</td>
</tr>
<tr>
<td><strong>wR</strong></td>
<td>0.0663</td>
<td>0.0409</td>
</tr>
<tr>
<td><strong>w</strong></td>
<td>l/[σ²(F)+0.0004F²]</td>
<td>l/[σ²(F)+0.000225F²]</td>
</tr>
<tr>
<td><strong>Final ΔF residual/eÅ⁻³</strong></td>
<td>0.62</td>
<td>0.50</td>
</tr>
</tbody>
</table>

* Details in common: scan type, θ-2θ; R, function minimized on F.

**Results**

**Crystal structures**

The ORTEP representations of the Fe₂OCl₂(tfpy)₂²⁺ and Fe₂OCl₂(epy)₂²⁺ cations are shown in Figs. 2 and 3, and the selected bond lengths and angles are listed in Table II. These two μ-oxo dimers with (tfpy) and (epy) ligands have a linear Fe–O–Fe structure as required by the center of symmetry at the bridging oxygen atom O(4). The Fe–μ-O bond distances are in the range 1.777(1)–1.781(1) Å, which are within the range of reported (μ-oxo)diron(III) complexes. Fe–N (pyridine, average 2.13 Å) and Fe–N (amine, average 2.20 Å) distances are also typical for the analogous (tpa) compounds [3]. It should be noted here that Fe–O₅ (etheral oxygen atoms of (tfpy) and (epy), which are located at the trans-position to the μ-oxo oxygen) distances are in the range 2.209(4)–2.264(2), which are very similar to that of Fe–N (pyridine) at the trans-position to the μ-oxo oxygen in the (tpa) complex, 2.263(3) Å [3]. These are indicating that coordination ability of an ethereal oxygen atom toward an iron(III) ion is comparable to that of pyridine nitrogen atom. The chloride ligands coordinate trans to the amine nitrogen on each iron center and anti to each other relative to the Fe–O–Fe axis. The Fe–Cl bond lengths are comparable to those of the reported
previously [3], These are indicating that structural features of three compounds with (tpa), (tpy) and (epy) are essentially the same to each other.

**Table II. Selected bond distances (Å) and bond angles (°).**

<table>
<thead>
<tr>
<th></th>
<th>Fe(l)—O(4)</th>
<th>Fe(l)—N(10)</th>
<th>Fe(l)—N(11)</th>
<th>Fe(l)—N(12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(tpy) Complex</td>
<td>2.285(2)</td>
<td>2.189(4)</td>
<td>2.198(4)</td>
<td>2.131(4)</td>
</tr>
<tr>
<td>(tfpy) Complex</td>
<td>2.209(4)</td>
<td>2.121(4)</td>
<td>2.121(4)</td>
<td>2.121(4)</td>
</tr>
<tr>
<td>(epy) Complex</td>
<td>2.209(4)</td>
<td>2.121(4)</td>
<td>2.121(4)</td>
<td>2.121(4)</td>
</tr>
</tbody>
</table>

**Table III. Turn-over numbers of the products (see Experimental section).**

<table>
<thead>
<tr>
<th></th>
<th>Cyclohexanol</th>
<th>Cyclohexanone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 min.</td>
<td>2 hours</td>
</tr>
<tr>
<td>(tpy)</td>
<td>1.2</td>
<td>4.6</td>
</tr>
<tr>
<td>(epy)</td>
<td>3.2</td>
<td>5.0</td>
</tr>
<tr>
<td>(tpa)</td>
<td>0.06</td>
<td>0.3</td>
</tr>
</tbody>
</table>

**Oxygenation of cyclohexane**

Time course of the formation of the oxygenated products are illustrated in Fig. 4, and the results are summarized in Table III, the turn-over numbers (molar ratio of product/iron(III) complex) of the products, cyclohexanol and cyclohexanone, are listed; it should be noted here that binuclear (tpa) complex exhibited negligible activity under the experimental conditions done. On contrast to this, the binuclear iron(III) complexes with (tpy) and (epy) showed high activity for the oxygenation of cyclohexane. The ability of the (tpy)-complex for oxygenation of cyclohexane was also observed under nitrogen atmosphere, while the turn-over numbers of the oxygenated products are almost the same as those observed under air.
Fig. 4. Time course of formation of cyclohexanol and cyclohexanone.
(A) cyclohexanol, (B) cyclohexanone.
\(\text{□ Fe}_2\text{OCl}_2(\text{tpa})_2(\text{ClO}_4)_2\),
\(\text{♦ Fe}_2\text{OCl}_2(\text{tfpy})_2(\text{ClO}_4)_2\),
\(\text{■ Fe}_2\text{OCl}_2(\text{epy})_2(\text{ClO}_4)_2\).

**Active species for decomposition of hydrogen peroxide**

The \(\text{H}_2\text{O}_2\) dismutation activity was tested by measuring the dioxygen evolution over a 60 min. period in acetonitrile with a complex: \(\text{H}_2\text{O}_2\) ratio of 1:100. As shown in Fig. 5, the iron(III) compound with (tpa) exhibited rather high activity for decomposition of hydrogen peroxide (ca. 70% of dioxygen of theoretical quantity evolved within an hour), but its activities of the (epy) and (tfpy) complexes are almost negligible. Both the results on the oxygenation reaction of cyclohexane and catalase-like function are clearly demonstrating that there exist two different kinds of active species in the solution, and that structure of an active species for decomposition of hydrogen peroxide is different from that active for oxygenation of cyclohexane [10]. In our previous paper, we have investigated the catalase-like function of the binuclear iron(III) compounds with \(\mu\)-alkoxo bridge, and concluded that an active species for decomposition of hydrogen peroxide should be of a dimeric (\(\mu^1\gamma^1\)-peroxo)diiron(III) structure [16]. Adduct II (shown below), and this consideration was supported by the recent work by Fontecave et al. [1(d)]; they observed a colored species formation when hydrogen peroxide was added to the binuclear iron(III) complex, which should be due to the Adduct II formation. According to the recent works [4,10], it is clear that structure of the \(\mu\)-oxo dinuclear iron(III) complexes is rather flexible in solution containing water or hydrogen peroxide, supporting that linear iron(III) complex with (tpa) can assume a bent peroxide adduct facilely, as shown below. This will explain the high catalase-like activity of the linear Fe(III)-(tpa) complex observed in this study, and is quite consistent with our observation [10] that a binuclear complex, \(\text{Fe}_2\text{O}(\text{CH}_3\text{COO})(\text{tpa})_2^{3+}\) [17] with bent structure also exhibits high catalase-like function.

![Dioxygen evolution catalyzed by iron(III) complexes](image-url)
As reported in the previous papers, the reactivity (electrophilicity) of the metal-peroxide adduct with side-on coordination mode is highly controlled by the phase of orbital of the electron-donors [6-a,b]. In the case of catalase-like function, two-electron transfer reaction from approaching hydrogen peroxide to the Adduct II is allowed to lead to evolution of dioxygen molecule, because phase of the orbitals of two reactants are coincident [18], as depicted below:

![Scheme I](image)

**Discussion**

*Active species for oxygenation reaction*

As described above, it seems reasonable to consider that an active species for oxygenation of cyclohexane should be different from Adduct II, and that the former should be inactive for decomposition of hydrogen peroxide. Fontecave *et al.* [4] and Que *et al.* [2] have considered that an iron(V)-oxo species derived from an iron-peroxide intermediate, must participate in the hydroxylation of cyclohexane. Arends *et al.* have paid attention to roughly equal yields of alcohol and ketone in the oxygenation reported by Que *et al.*, since this is symptomatic of a Russell-type termination of two secondary peroxide radicals;

\[
2\text{CHOO} \rightleftharpoons \text{CHOOOCH} \rightleftharpoons \text{CHOH} + \text{C} = \text{O} + \text{O}_2
\]

![Scheme II](image)

and they proposed that iron(III)/alkyl hydroperoxide system (ROOH) oxidize alkanes via alkoxyl radicals rather than via the postulated high-valent iron-oxo species. But their consideration may not be applied to the present cases, because oxidant is hydrogen peroxide. Fish *et al.* have reported that cyclohexyl hydroperoxide, which may form from dioxygen and cyclohexyl radical derived through hydrogen atom abstraction of cyclohexane by high-valent iron-oxo species, exists in the solution containing binuclear iron(III) and hydrogen peroxide, and proposed that formation of cyclohexanol and cyclohexanone occur through the decomposition of the cyclohexyl hydroperoxide. We in this study have observed that the yields of the oxygenated products in the solution bubbled by nitrogen gas are essentially the same as those bubbled by dioxygen molecule, and our results are very similar to that reported by Fontecave *et al.* [4]. These are suggesting that dioxygen molecule does not participate in the oxygenation of cyclohexane in our present systems.

Recently, we have observed that an iron(III)-peroxide adduct with \(\eta^1\)-coordination mode exhibits high electrophilic nature [6-d], leading to facile interaction between the peroxide adduct and the carbon atom in the organic moiety, giving formation of C–O bonding [6-c,d]. This seems to be consistent with the discussion proposed for the particulate methane monooxygenase [19] and heme-oxygenase [20]. Thus, we have assumed that a peroxide-iron(III) species, Adduct I should be closely related with activity of the (tftpy) complex for oxygenation of cyclohexane, since the (tpta)-complex shows negligible activity for oxygenation of cyclohexane.

*Results on MO calculations and activation of peroxide ion*

At first, we have performed the MNDO/AM1 calculations for the organic moieties, tetrahydrofuran, pyridine, and ethylmethylether, and the positional parameters of the compounds were optimized by the same computer program. In Fig. 6, orbital shapes of the HOMO and LUMO are illustrated: HOMO is mainly consisted of \(p_z\)-orbital of the ethereal oxygen atom in the cases of tetrahydrofuran and methylethylether. We already reported the calculated results on the Fe(NH$_3$)$_5$($O_2^{2-}$) performed by EHMO method [10]; in this situation it is clear that \(d_{xy}p_z\) orbital can interact with both \(\pi^*\)- and \(\sigma^*\)-orbitals of the peroxide adduct with \(\eta^1\)-coordination mode and it should be noted here that the \(d_{xy}p_z\) orbital, which is interacting with the peroxide ion, contains a
considerably parts of $p_x$- and $p_z$-orbitals of O1 atom and $p_z$- but negligible $p_x$-orbitals of O2 atom; the appearance of $p_z$-orbitals of O1 and O2 with the same signs represents the mixing of $\sigma^*$-orbital into the $d_{x^2-y^2}$ [10]. Since the $d_{x^2-y^2}$ is half-filled, this orbital can interact with the occupied orbital of the organic substrate at the O1 or O2 position as indicated by the arrow in the figure below, and this was experimentally confirmed in several papers, i.e., benzene ring neighboring at the iron(III) ion was facilely hydroxylated to yield phenol in the presence of hydrogen peroxide [21], and also heme-oxygenase reaction [20].

\[ \text{Scheme III} \]

It seems quite likely that a hydroperoxide adduct formation may proceed in all the cases including (tpa), (tfpy) and (epy) ligands as shown below.

\[ \text{Scheme III} \]

Crystal structural determinations suggest that a hydroperoxide ion should exist in the plane which contains the plane of organic moieties, such as pyridine or tetrahydrofuran ring as shown in Scheme IV; thus the EHMO calculation were performed for the Fe(NH$_3$)$_4$(tetrahydrofuran)($\text{HO}_2^-$) as a model compound for Adduct I, where tetrahydrofuran ring and peroxide ion are in the same plane ($x$-$y$ plane).

\[ \text{Scheme IV} \]

The results obtained by the EHMO method including organic moiety clearly demonstrated that the hydroperoxide ion coordinating to an iron(III) ion in Scheme III can interact with the tetrahydrofuran ring (see Fig. 7), giving a pentacoordinate carbon species formation (see Adduct I), which is due to the electrophilic reactivity at O2 site of the hydroperoxide adduct as described above. It should be noted here that in addition to the in-plane interactions (C1 atom can approach to O2 atom through orbital interaction, see Fig. 8), $\pi$-interaction between the $p_z$-orbitals of peroxide ion and tetrahydrofuran ring is noteworthy (see orbital A in Fig. 8), which is attained via interaction with a half-filled d-orbital ($d_{xz}$, $d_{yz}$). This should contribute rather stabilization of energy of HOMO of tetrahydrofuran ring, leading to the stronger interaction between O2 and C1 atoms. The interaction between the occupied orbitals of the tetrahydrofuran ring and the peroxide adduct (see Fig. 8) should lead to electron transfer from the organic moiety to the peroxide ion, making the heterolytic O–O cleavage of the peroxide adduct to be more facile. Two hydrogen atom, which are located at the upper and lower sites of the tetrahydrofuran ring are also contributing to the binding with peroxide ion via hydrogen-bonding. The same results were also observed in the case of dimethylether instead of tetrahydrofuran. The assumption for the possible interaction between C1 of tetrahydrofuran ring and peroxide adduct may be supported by the fact that $\alpha$-carbon of the THF is easily oxygenated in the oxidation reaction [22]. In the case of (tpa) complex, $\pi$-interaction between the hydroperoxide ion and pyridine ring, as...
suggested for the tetrahydrofuran ring, is negligible (see Supplementary data). This may be due to that HOMO of pyridine ring does not contain the p- orbital of nitrogen atom. In addition to this, O2 atom of the peroxide ion cannot approach to the carbon atom of the pyridine ring because of the presence of hydrogen atom (see Scheme V); this situation may make the hydroperoxide adduct formation as assumed for the (tfpy) complex to be less favorable in the (tpa)-complex, and rather may lead to a peroxide adduct formation of (μ-η1:η1-peroxo)diiron(III) species, which is consistent with high catalase-like activity of this compound.

**Fig. 8. Interaction between occupied orbital of THF molecule and singly-occupied d,y,z orbital.**

**Oxygenation reaction of cyclohexane**

As shown in the previous section, the hydroperoxide ion coordinating iron(III) ion can interact with the tetrahydrofuran ring or methylethylether moiety to induce facile Adduct I formation. Based on these facts, we would like to propose that the oxygenation reaction of cyclohexane catalyzed by...
the Fe(III)-(tfpy) and hydrogen peroxide may proceed as follows; Adduct I described above acts as an electrophile and interacts with the electrons of bonding orbitals of substrate at the O1-site (see Scheme VI, in the scheme approach of HOMO of the methane molecule [24] is depicted). Since the metal d-orbital contains character of $\sigma^*$-orbital of peroxide ion, approach of HOMO of methane induces the more facile cleavage of O–O bond in the peroxide adduct; heterolytic cleavage of O–O bond of the peroxide adduct may lead to formation of iron(III)-oxygen(atomic)–hydroxide species [23], and this species may be alternately written as a high valent iron-oxo species. Thus, both the electronic interaction between the hydroperoxide ion and the tetrahydrofuran ring and also the approach of methane to O1 atom of the peroxide adduct may enhance formation of a high-valent iron-oxo species with concerted heterolytic O–O bond cleavage, giving methane-oxygen linkage, and this should give an oxygenated product, methanol [10]. The formation of cyclohexanol and cyclohexanone may be elucidated by the same ways as described for methanol.