



Article 'Oxygen-Consuming Complexes'–Catalytic Effects of Iron–Salen Complexes with Dioxygen

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Abstract: [(salen)Fe^{III}]⁺_{MeCN} complex is a useful catalyst for cyclohexene oxidation with dioxygen. As the main products, ketone and alcohol are formed. In acetonitrile, [(salen)Fe^{II}]_{MeCN} is rapidly oxidized by dioxygen, forming iron(III) species. Voltammetric electroreduction of the [(salen)Fe^{III}]⁺_{MeCN} complex in the presence of dioxygen causes the increase in current observed, which indicates the existence of a catalytic effect. Further transformations of the oxygen-activated iron(III) salen complex generate an effective catalyst. Based on the catalytic and electrochemical results, as well as DFT calculations, possible forms of active species in *c*-C₆H₁₀ oxidation have been proposed.

Keywords: dioxygen activation; cyclohexene oxidation; electrochemical catalytic effect; iron-tetradentate complexes; reactive oxygen species

1. Introduction

Catalytic oxidation of olefins is still a fundamental process in organic chemistry, with many industrial applications. In particular, allylic oxidation is a key transformation in different synthetic strategies [1–6]. For environmental and economic reasons, catalytic oxidation reactions with dioxygen as an oxidant, which take place under mild conditions, are extremely valuable [7–10]. Nature has provided oxygen available in the air—an abundant and renewable chemical oxidant. The ground state of molecular dioxygen, due to its triplet spin, is diradical, with two unpaired electrons characterized by parallel spins [11–14]. Despite the radical nature, the paramagnetic oxygen molecule, contrary to expectations, does not react in a manner typical for radicals. It is very passive toward neutral, diamagnetic substrates present in both biological and chemical systems. For such a reaction to progress, it is necessary to change the spin, which not only requires energy but also time. However, the lifetime of the active complex is significantly shorter, which is insufficient for a spin change to occur during its lifetime, hence such reactions are called spin-forbidden [11,12,14]. For this reason, molecular oxygen has to be activated in order to react with organic compounds. The complexes of transition metals, which have multiple spin and oxidation states available, can activate dioxygen for the oxygenation of organic substrates [15,16]. In the process, highly reactive, thermally unstable, and metal-oxygen intermediates are generated via electron and proton transfer reactions. Particularly for iron, many open-shell spin states are possible, depending on the oxidation state of Fe. High-spin (HS) iron(II) is considered to be probably the most important spin state when it comes to the activation and binding of dioxygen [16]. Many mononuclear iron enzymes non-related to heme chemistry activate molecular oxygen, forming very reactive iron-peroxo (Fe^{III}–OOH, Fe^{III}–O₂⁻) or iron-oxo (Fe^{IV}=O) species as oxidants [16–21]. Dioxygen reacts in numerous ways with biological non-heme iron centers. For α -ketoglutarate-dependent dioxygenases and halogenases,



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). peptidylglycine α -hydroxylating monooxygenases, and cysteine dioxygenases, activation in non-heme metalloenzymes starts with a reduced metal center Fe(II) and passes through several intermediates such as metal-superoxo, -peroxo, -hydroperoxo, and -oxo ones, some of which are accountable for substrate oxidation reactions [22,23]. The formation of the iron-O₂ adduct reported as an iron(III)–superoxo species is the first step in molecular oxygen activation and occurs via O₂ coordination to the iron(II) center. In these species, the electron from the iron center is transferred to the oxygen molecule [18,20,24–29]. However, characterizing superoxo species has proven to be a difficult task, and no such intermediate has been observed for mononuclear nonheme iron complexes up to 2014 when a mononuclear Fe^{III}(O₂⁻) complex was described [30]. Additionally, the activation of dioxygen by a non-heme iron(II) catalyst supported by proton and reductant participation can lead to the formation of a reactive adduct iron(IV)=oxo [20,30–33]. From this intermediate, other reactive forms of catalysts, such as Fe^{III}-OH or Fe^{III}-OOH, can be formed [34,35].

Iron-based catalysts have attracted much attention due to iron's abundance, nontoxicity, environmental benignity, and low price [36–38]. These catalysts have been used in many chemical transformations [39–42]. The iron(III)/(II)-salen-like complex is known as a catalyst used for C-C cross-coupling reactions [43], for DNA cleavage [44–47], as active compounds with antitumor applications [48], for the fabrication of biosensing electrodes [25,49], for the regulation of radical concentration in the atom transfer radical polymerization (ATRP) method [50], for the photoremediation of pollutants [51], as inexpensive precursors for the synthesis of metal- and nitrogen-containing carbon nanomaterials [52], and as solid-supported metal complexes for heterogeneous catalysis [53]. According to the literature, iron(III) salen complexes activated by different oxidants were examined for the oxidation reactions listed in Table 1.

Cyclohexene is a compound that is frequently exploited as a model substrate in preliminary catalytic studies. Due to the presence of single C–H and double C=C bonds susceptible to oxidation, studies on its reactivity serve as a good starting point for the discussion of the reaction mechanism and reactivity of this compound as well as other chemicals [54]. Previously, we found that in acetonitrile (MeCN) labile iron(II) complexes with 2,2'-bipyridine (bpy), $[Fe^{II}(bpy)_2^{2+}]_{MeCN}$ activate dioxygen for the oxidation of cyclohexene [55], to ketone and alcohol. Moreover, the complexes catalyze the oxidation of limonene [56] and dealkylation of $N_{i}N$ -alkylanilines [57] by dioxygen. We have also reported [58] that manganese(III) complexes in combination with tert-butyl hydroperoxide (t-BuOOH) activate dioxygen (O_2) to oxygenate cyclohexene ($c-C_6H_{10}$) to its ketone, alcohol, and epoxide. The product profiles depend on the ligand and solvent matrix. With pyridine-2-carboxylate, 2,2'-bipyridine, or triphenylphosphine oxide as ligands in pyridine/acetic acid (2:1 molar ratio), the dominant product is the ketone c-C₆H₈(O), while Schiff-base complexes produce $c-C_6H_8(O)$, $c-C_6H_9(OH)$, and epoxide in almost equal yields. However, in acetonitrile, $c-C_6H_8(O)$ is the dominant product for the investigated complexes. Furthermore, we have demonstrated the manganese(II) complex with the pentadentate ligand can activate dioxygen for the oxidation of cyclohexene [54].

In addition to the oxidation of cyclohexene, catalyzed by a complex activated with different oxidants (Table 1), leading to the production of alcohol and ketone [59,60], an auto-oxidative path of cyclohexene oxidation is also possible, in which transition metal complexes mainly act as activators of radical reactions [61]. In the paper [61], several iron(III) chloro- complexes with *N*,*N'*-disalicylidene-1,2-diaminoethane (H₂salen) derivatives bearing electronegative substituents have been described as catalysts for the aerobic oxidation of cyclohexene. These transformations primarily produced allylic oxidation products (cyclohex-2-en-1-one, cyclohex-2-en-1-ol). The main product of an auto-oxidative reaction was usually ketone, but alcohol and epoxide were also observed [61,62]. The same products were formed during cyclohexene oxidation in the presence of molecular dioxygen and a bimetallic gold-iron nanocatalyst supported on commercial titania [63].

Substrates	Products	Reaction	Solvent	Oxidant	Refs.
cyclohexene	cyclohexenone and cyclohexenol, epoxide was formed in small amounts	cyclohexene oxidation	MeCN	PhIO	[59]
cyclohexane	cyclohexanone and cyclohexanol	cyclohexane oxidation	MeCN	HOOH, TBHP	[64]
natural propenyl- benzenes (safrol, isosafrol, anethol, eugenol, and isoeugenol)	conversion of these substrates into epoxides	propenylbenzenes epoxidations	MeCN	НООН, ТВНР	[65]
organic sulfur compounds	sulfoxides	oxidation	MeCN	PhIO, HOOH	[18,66-68]
various olefins	epoxides, ketones, and alcohols	oxidation	MeCN	НООН	[69]
ring-substituted anilines	azobenzenes transformed to azoxyben- zenes, and oligomers of anilines	oxidation	MeCN	НООН	[19]
amino acids	corresponding ketimines	oxidative decarboxylation and deamination	75% DMF– 25% water solvent mixture	HOOH, t-BuOOH, PhIO, MCPB, PMS	[70]

Table 1. Iron (III) salen complexes as catalysts for the oxidation of organic compounds.

The lower stability constant of [(salen)Fe^{II}], amounting to $3 \cdot 10^{17} \text{ M}^{-1}$ [25], compared with the one characteristic of very stable [(salen)Fe^{III}]⁺ [71], equal to $7.1 \cdot 10^{25} \text{ M}^{-1}$, favors electron transfer reactions between electron acceptors such as dioxygen and [(salen)Fe^{II}], resulting in [(salen)Fe^{III}—-O₂] complexes [25].

According to the literature, there are many examples of the synthesis of the complex of iron(III) salen [20,47,64,65,72], and only a few examples of the synthesis of the iron(II) salen complex [73]. The complex [(salen)Fe^{III}]⁺, in most of those articles, was synthesized according to the procedure of Matsushita et al. (1982) according to which ferric chloride and the salen ligand in a 1:1 molar ratio were dissolved in absolute CH₃OH, and the resulting mixture was heated to reflux under an inert gas atmosphere for about 2.5 h. Solid [(salen)Fe^{III}]Cl was isolated by filtration and then used for catalytic purposes [74]. The synthesis of the [(salen)Fe^{II}] complex was carried out under an inert gas atmosphere, an appropriate iron(II) salt, at a low temperature [73]. Moreover, transition metal ion-Schiff base complexes were prepared in situ in a straightforward and catalytically useful reaction between the ligand and selected transition-metal ions [75].

The above findings encouraged us to investigate the oxidation of cyclohexene by dioxygen catalyzed by several iron(II/III) complexes with salen and its derivatives.

2. Results and Discussion

2.1. Catalytic Tests

We have found that $[(salen)Fe^{II}]_{MeCN}$ (prepared in situ by mixing Fe(ClO₄)₂ and salen in an inert gas atmosphere in a Schleck flask) activates dioxygen for the oxygenation of

cyclohexene. The corresponding ketone [cyclohex-2-en-1-one] and alcohol [cyclohex-2-en-1-ol] are the main products, and epoxide [cyclohexene oxide] is formed in much smaller amounts (Scheme 1).



Scheme 1. Products of cyclohexene oxidation.

The results obtained for different substrate concentrations and dioxygen pressures are presented in Table 2. The reaction yields obtained when air ($p_{O2} = 0.2$ atm) was used as an oxidant are higher (except for the substrate concentration equal to 4 M) than those observed in the presence of pure dioxygen ($p_{O2} = 1$ atm). Therefore, air ($p_{O2} = 0.2$ atm) was used as an oxidant in subsequent experiments. The concentration of cyclohexene was determined to be equal to 1 M. Table S1 shows the dependence of product yields on catalyst concentrations. The maximum reaction yield is observed for catalyst concentrations ranging from 1 to 2.5 mM, whereas for concentrations higher than 5 mM, no oxidation products are observed. This suggests that at higher catalyst concentrations, the reaction with dioxygen leads to rapid deactivation of the catalyst, probably due to μ -oxo adduct formation.

Substrate Concentration, M	Ketone, mM	Alcohol, mM	Epoxide, mM	TON
(a)				
0.5	9.4	4.2	0.1	13.7
1	53.6	26.1	0.9	78.8
2	90.5	38.0	0.6	129.2
3	128.6	49.9	0.6	179.1
4	190.4	53.1	1.0	244.4
(b)				
0.5	2.8	0.7	0.0	3.2
1	27.8	12.6	0.4	40.8
2	56.5	24.5	0.6	81.6
3	111.9	47.4	1.0	160.2
4	215.0	82.5	1.3	298.8

Table 2. Oxidation of cyclohexene with (a) air ($p_{O2} = 0.2$ atm) or (b) dioxygen ($p_{O2} = 1$ atm) in acetonitrile at room temperature (23 ± 1 °C) catalyzed by 1 mM iron-salen species for different substrate concentrations. Reaction time 24 h.

TON—product molecules per catalyst molecule.

The product concentration profiles within 12 h of the experiment run at room temperature (23 \pm 1 °C, curves 3, 4, and 6) and at elevated temperature (55 °C, curves 1, 2, and 5) using a 1 M substrate, 1 mM catalyst, and air (p_{O2} = 0.2 atm) are presented in Figure 1. The concentrations of each product formed at 55 °C were almost double in comparison to the ones observed at room temperature.

It is noteworthy that the formation of the products at room temperature was preceded by the induction period. To further explore the nature of the process, additional experiments were performed. The catalyst was exposed either to air (for 3 h) or the solution of the catalyst was aerated. Alternatively, 1 mM *t*-BuOOH was added before the substrate addition and the standard procedure for oxidation was continued. In both cases, the induction period was not observed. The concentrations of products after the 5 h run of the oxidation process were analogous to those observed after 8 h of the process in which 3 h induction period took place. In contrast, when 1 mM HOOH instead of *t*-BuOOH was added, the oxidation process was completely inhibited. The findings described above indicate that the formation of reactive species at room temperature is a slow process and raises questions about its stability. Obviously, the catalyst is deactivated by strong oxidants (HOOH). In the long-term experiments conducted, we observed the plateau on the concentration profiles vs. time starts to form after 6 to 8 days (Figure S1). After 11 days of the process, the catalysts began to decompose, and the formation of a brown precipitate was observed.



Figure 1. Dependence of product concentrations for ketone (1), alcohol (2), and epoxide (5) at 55 $^{\circ}$ C and ketone (3), alcohol (4), and epoxide (6) at room temperature on time for the oxidation of 1 M cyclohexene with air catalyzed by 1 mM iron-salen species in acetonitrile.

Alkyl hydroperoxides do not form during the oxidation process. This suggests that an autocatalytic path is excluded. To confirm this finding, the Shul'pin test was performed, and in the presence of hydroperoxide in the solution, it should react quantitatively with the added triphenylphosphine to form alcohols and O=PPh₃ [62]. Ph₃P was added to the final reaction mixture; however, compared to conditions without Ph₃P, no significant concentration of alcohol was observed.

The catalytic activity of $[(salen)Fe^{II}]_{MeCN}$, $[(salen)Fe^{III}]ClO_{4MeCN}$, and $[(salen)Fe^{III}]Cl_{MeCN}$ were also compared, and the results are presented in Table S2. The last listed complex was chosen because of its known lack of catalytic activity towards the process investigated [61]. It is characteristic that the yields of the products obtained by the use of Fe^{III} are lower in comparison to Fe^{II}. This indicates that the oxidation of the [(salen)Fe^{II}]_{MeCN} complex by dioxygen is not a simple metal-centered electron transfer, and the reaction of cyclohexene oxidations catalyzed with the salen complex synthesized from iron(II) salt was the most effective.

2.2. Electrochemical Research

The above-presented results indicate that $[(salen)Fe^{II}]_{MeCN}$ is a promising catalyst for dioxygen activation. However, the nature of the reactive species in the system is uncertain. As follows from voltammetric measurements (Figure 2), the $[(salen)Fe^{II}]_{MeCN}$ complex is rapidly oxidized by dioxygen. This raises a question about the active form of the catalyst in the cyclohexene oxidation processes. Even under an argon atmosphere ((Fe^{II}(ClO₄)₂ was dissolved in rigorously deoxygenated acetonitrile and then the deoxygenated solution of salen was introduced to the electrochemical cell and a cyclic voltammogram was recorded), the reduction peak is observed in the first cathodic scan. However, the oxidation peak of the Fe(II)-complex is still present in the first anodic scan. This fact suggests that the Fe(II)-complex was partially oxidized by the traces of dioxygen, and both the reduced and the oxidized forms of the complex are present in the solution. Any excess of dioxygen causes the Fe(II)-complex to disappear, and no anodic peak is observed.



Figure 2. Cyclic voltammograms in acetonitrile (0.1 M Et_4NClO_4) for 5 mM [(salen)Fe^{II}]_{MeCN} in rigorously deoxygenated (by conventional method) solution: The black solid line shows the cathodic, while the red dash line shows the anodic scan, which was recorded first. Scan rate, 0.1 Vs⁻¹, GCE (0.008 cm²); SCE vs. NHE, +0.242 V.

The aeration of the [(salen)Fe^{II}]_{MeCN} solution causes the rest potential to be shifted about 0.5 V toward more positive values and a substantial increase in the high of the reduction peak, which is irreversible. This is analogous to the case when [(salen)Fe^{III}]⁺_{MeCN} is reduced in the presence of dioxygen (Figure 3). In contrast, although [(salen)Fe^{III}]Cl is reduced at the same potential, it gives no such effect.



Figure 3. Cyclic voltammograms in acetonitrile (0.1 M Et₄NClO₄) for (**a**) 5 mM [(salen)Fe^{III}]⁺_{MeCN} and (**b**) 5 mM [(salen)Fe^{III}]⁺_{MeCN} in a dioxygen atmosphere. Scan rate, 0.1 Vs⁻¹, GCE (0.008 cm²); SCE vs. NHE, +0.242 V, cathodic scans.

This behavior is characteristic for electrochemical catalytic processes, in which a reduced form of an electroactive species is reoxidized in a chemical reaction with a solution component giving back the oxidized form (Scheme 2).



Scheme 2. Electrochemical catalytic process.

Since the salen complex synthesized from the iron(II) salt [(salen)Fe^{II}]_{MeCN} is a better catalyst than iron(III) [(salen)Fe^{III}]⁺_{MeCN}, it should be expected that the oxidation process carried out during continuous reduction of the oxidized catalyst will produce a better yield. Electrolysis running at -0.3 V vs. SCE (a slightly more negative potential than that for the reduction of the oxidized catalyst) in the presence of cyclohexene yields only traces amounts of the corresponding products. During electrolysis, the current intensity decreased from 4.5 mA to 0.2 mA within 60 min, as under these conditions, the electrode process likely resulted in decomposition of the complex at the surface of the electrode. This is confirmed by the results of multiple CV scans in the range +0.35 to -0.6 V, where a sharp decrease of current was observed (Figure S2).

The presented results raise the question of the nature of reactive species resulting from the reaction of transition metal complexes with dioxygen. As indicated by the cyclic voltammograms registered during the deoxidation of the previously oxygenated catalyst solution, the oxidation of the [(salen)Fe^{II}]_{MeCN} complex by dioxygen is not a simple metalcentered electron transfer process (Figures S3–S5). In the tested range of potentials, salen complexes with FeCl₃ do not react with O₂ (Figure S4), Fe(ClO₄)₃ salts easily react with dioxygen, binding it in a reversible way; both the binding and oxygen release reactions are very fast (Figure S3), while complexes formed with Fe(ClO₄)₂ immediately react with dioxygen, and this reaction is not completely reversible. Even after 45 min of deoxidation of the previously oxygenated solution, no initial peak currents were registered (Figure S5).

In the catalytic tests performed, the induction period was determined, and because of that, CV curves were recorded in the 1 mM iron(II)-salen catalyst solution in the atmosphere of air and dioxygen after selected reaction times (Figure 4).



(a) air ($p_{02} = 0.2$ atm)

(b) dioxygen ($p_{02} = 1 atm$)

Figure 4. Cyclic voltammograms in acetonitrile (0.1 M Et₄NClO₄) for iron species formed in a reaction of 1 mM [(salen)Fe^{II}]_{MeCN} with O₂ over time. (**a**) Air ($p_{O2} = 0.2$ atm) atmosphere, (**b**) dioxygen ($p_{O2} = 1$ atm) atmosphere. Scan rate, 0.1 Vs⁻¹, GCE (0.008 cm²); SCE vs. NHE, +0.242 V, cathodic scans. Oxygenated catalyst in time after I—0 min (immediately after aeration), II—5 min, III—30 min, IV—1 h, V—3 h.

The results collected in Figure 4 demonstrate that the reduction peak formed in an oxygen atmosphere at a potential of 0 V decreases with reaction time (i.e., the time after the catalyst was mixed with the appropriate oxidant) and disappears after 3 h of reaction in the air (Figure 4a), while in the case of the dioxygen atmosphere ($p_{O2} = 1$ atm) it is still present but shifts towards more negative potentials (Figure 4b). In addition, whilst the height of the peak at 0 V decreases, the height of the peak registered at -0.3 V increases, probably because a new active form of the dioxygen-activated catalyst is formed. The addition of the substrate—cyclohexene—to the reaction mixture (Figure S6) does not affect the height of the described peaks. Further electrochemical investigations were performed for a 1 mM concentration of iron complexes, because the concentration was optimal for catalytic investigations. In the deoxygenated 1 mM solution of the [(salen)Fe^{II}]_{MeCN} complex, the dependencies of the cathodic (-0.1 V) and anodic (about 0 V) peak currents on the square

root of the polarization speed were determined (Figure S7). The following polarization rates were used: 50, 100, 250, 500, 750, and 1000 mV/s. The linear dependencies of i_k and i_a on $v^{1/2}$ (Figure S7) show that the processes responsible for the occurrence of these peaks are controlled by the diffusion rate of the electroactive substance to the electrode surface, and no chemical reaction takes place.

According to literature reports [18,66,70,76], the [(salen)Fe^{IV}=O] complex is formed when iodosylbenzene is added to the solution of [(salen)Fe^{II}]. Figure S8 shows a cyclic voltammetric curve recorded in a 1 mM solution of [(salen)Fe^{II}] with excess PhIO. The voltamperogram presents the reduction peak at a potential of about -0.3 V (Figure S8a), which corresponds to the reduction of the [(salen)Fe^{IV}=O] complex.

The addition of a proton-donating substance (HClO₄) shifts the reduction peak to more positive potentials (Figure S8b), which can be explained by the incorporation of H^+ in the process [Equation (1)]:

$$[(salen)Fe^{IV}=O] + H^{+} + e^{-} \rightarrow [(salen)Fe^{III}-OH]$$
(1)

The peak at a potential of -0.3 V, formed over time in the oxygenated [(salen)Fe^{II}] solution (Figures 4 and S6), is probably related to the formation of the oxo form of the catalyst [(salen)Fe^{IV}=O]. The formation of iron(IV)oxo complexes with the salen ligand has already been described in the literature [18,66,70,76].

2.3. DFT Calculations

Furthermore, quantum chemistry methods were used to better understand the mechanism of the processes taking place during the oxidation of cyclohexene with molecular oxygen in the presence of the $[(salen)Fe^{II}]_{MeCN}$ complex. Some studies show that the catalytic capacity of iron–salen complexes depends on the kind of iron salt used for the synthesis of the complex [25,71]. For this reason, thermodynamic calculations (energies, enthalpies, and free energies) were performed for salen complexes formed with iron(II) and iron(III) ions derived from chlorates and chlorides (Table S3). Geometry optimization and thermodynamic calculations for the catalyst models presented in Table S3 were performed for their possible high-, intermediate, and low-spin configurations. Based on the performed catalytic and electrochemical measurements supported by literature data [25,30,68,77], the most-probable mechanism of dioxygen of activation by iron(II) salen complexes is shown in Scheme 3.



Scheme 3. Proposed sequence of reactions for the activation of dioxygen by iron salen catalysts.

The [(salen)Fe^{II}] with a weaker stability constant (compared with complexes of iron(III)) reacts with dioxygen to form an intermediate [(salen)Fe^{III}—-O₂]. Next, the intermediate reacts with an electron (e.g., from the iron(II) catalyst, which is correspondingly oxidized to the form of iron(III)) and a hydrogen atom available in the solution (traces of water contained in the solvent, or in organic cyclohexene substrate) yielding, after further transformations, an active catalyst–salen iron(IV)-oxo complex (Scheme 3).

To explain the differences in the efficiency of oxidation of cyclohexene catalyzed by salen complexes with various iron salts, Gibbs free energies were calculated for subsequent steps of catalyst activation by a hydrogen atom (Table 3). $\Delta_r G$ were calculated first (based on Table S4), to exclude reactions not possible under normal conditions. Subsequently, the reaction mechanism for the most promising catalyst was modeled.

Table 3. Reaction Gibbs free energy for catalyst activation modeled as an attachment of a hydrogen atom to the complex.

Line	Reactions:	Δ _r G [kJ/mol]
1	[(salen)Fe]OO \xrightarrow{H} [(salen)Fe]OOH	-307.9
2	(Cl)[(salen)Fe]OO \xrightarrow{H} (Cl)[(salen)Fe]OOH	-280.3
3	$(ClO_4)[(salen)Fe]OO \xrightarrow{H} (ClO_4)[(salen)Fe]OOH$	-300.0
4	$[(salen)Fe]=O \xrightarrow{H} [(salen)Fe]OH$	-385.3
5	(Cl)[(salen)Fe]=O \xrightarrow{H} (Cl)[(salen)Fe]OH	-371.1
6	$(ClO_4)[(salen)Fe]=O \xrightarrow{H} (ClO_4)[(salen)Fe]OH$	-384.1

Based on the analysis of the calculated Gibbs free energies contained in Table 3, it can be concluded that both in the case of molecules of the peroxide catalyst as well as ironoxo complexes derived from the three tested iron salts, the hydrogen atom is attached in spontaneous reactions ($\Delta rG < 0$). Comparing the data from catalytic tests, electrochemical experiments, and DFT calculations, it is possible to single out [(salen)Fe^{IV}=O] as the most likely active form of the catalyst for the cyclohexene oxidation reaction in this work.

Assuming that the [(salen)Fe^{IV}=O] complex is the active catalyst in the oxidation of cyclohexene, the corresponding reaction was modeled. The reaction profile for cyclohexene (CH) hydroxylation by ^{1,3,5}[(salen)Fe^{IV}=O] is displayed in Figures 5 and S9, and related thermodynamic data are collected in Table S5.



Figure 5. Relative energies with ZPE correction (Table S5) of singlet (**1**, **gray**), triplet (**3**, **black**), and quintet (**5**, **green**) for the reaction of cyclohexene oxidation catalyzed by [(salen)Fe^{IV}=O] to alcohol. For the initial complexes **S** (in three various spin states) the values of starting relative energies are given next to the respective line. The legend of used symbols: S—substrates: [(salen)Fe=O)]+H-C₆H₉, TSI—[(salen)Fe—O—H-C₆H₉], PI—products1: [(salen)Fe-OH)]+C₆H₉, TSII—[(salen)Fe—O(H)—C₆H₉], PII—products2: [(salen)Fe]+C₆H₉OH.

The reactants, ${}^{1,3,5}[(salen)Fe^{IV}=O] + C_6H_9-H$ (S), following two transition states (TSI, TSII) transform into alcohol and [(salen)Fe^{II}] products (PII). The activation energies of TSI for singlet, triplet, and quintet are respectively 70.5, 49.0, and 15.4 kJ/mol (Figure 5 and Table S5); similarly, relative Gibbs free enthalpies grow in the same order (Figure S9). Analysis of the TSI activation energy shows that the quintet is the most favorable because it has the lowest barrier at TSI. Although the substrates (S) in the quintet are about 13 kJ/mol higher than the S in the triplet, this is only a slight difference and can be considered energy equivalent. For quintet TSII, the activation energy is also the lowest, therefore in reactions of cyclohexene oxidation catalyzed by [(salen)Fe^{IV}=O], quintet channels are energetically privileged.

3. Materials and Methods

3.1. Chemicals

The reagents for the investigations and syntheses were purchased from commercial sources and used without further purification. The solvent for all experiments was acetonitrile (99.93+ %, HPLC grade) purchased from Aldrich. High-purity argon gas was used to deoxygenate the solutions. Tetraethylammonium perchlorate (Et₄NClO₄, TEAP, GFS Chemicals) was dried in vacuo over CaSO₄ for 24 h before use. Iron (II) and iron (III) perchlorates, Fe(ClO₄)₂·6H₂O and Fe(ClO₄)₃·6H₂O, were obtained from GFS Chemicals, whereas iron (III) chloride, FeCl₃, was from Aldrich. Organic substances, including cyclohexene (99%), 2cyclohexen-1-one (95+ %), 2-cyclohexen-1-ol (95%), cyclohexene oxide (98%), and biphenyl (PhPh, 99+ %), as well as the salen ligand (98%) [*N*,*N*'-bis(salicylidene)ethylenediamine)], were purchased from Aldrich. Hydrogen peroxide (50% water solution) and *tert*-butyl hydroperoxide in nonane were obtained from Aldrich.

3.2. Methods

The reaction products were separated and identified with a Hewlett-Packard 4890A series gas chromatograph equipped with an HP-1 capillary column (cross-linked methyl-silicone-gum phase, 30 m \times 0.53 mm id). In GC analysis, the temperature was maintained at the initial value of 35 °C for 4 min, then increased at the rate of 30°/min to 220 °C and left unchanged for 8 min. The analysis time was 18.16 min. The sample was injected into the precolumn, and the temperatures of the injector and detector were 250 °C and 300 °C, respectively.

A three-electrode potentiostat (Princeton Applied Research Model 273A) was used to record the cyclic voltammograms. Experiments were conducted in a 2-mL electrochemical cell with the provision to control the presence of dioxygen with an argon-purge system. The working electrode was a 1-mm-diameter glassy carbon electrode EE040 in PEEK (Cypress Systems, a Division of ESA, Inc.), the auxiliary electrode was a platinum wire, and the reference electrode was an Ag/AgCl wire in an aqueous tetramethylammonium chloride solution that was adjusted to produce a potential of 0.00 V vs. SCE. The reference electrode was contained in a Pyrex tube with a Vycor tip [78]. Before each experiment, the working electrode was polished using a Buehler Micropolish Alumina Gamma 3B and Buehler Microcloth polishing cloth, then rinsed with deionized H₂O and dried.

In preparative experiments, the appropriate amounts of metal salt [Fe(ClO₄)₂·6H₂O, Fe(ClO₄)₃·6H₂O, or FeCl₃] and the ligand were combined in acetonitrile (and mixed under Ar atmosphere for 1 h). Then the solution was saturated with dioxygen (O₂, 1 atm) or air (O₂, 0.2 atm) or high-purity argon gas (O₂, 0 atm) for blank experiments. The appropriate gas, saturated with acetonitrile, was passed over the solution to maintain a constant concentration of dioxygen in the solution. The next step was substrate addition (total volume = 5 mL) to the reaction cell (a 25 mL vial with a cut-out cap and a Teflon-faced septum). The reactions were allowed to proceed for 24 h with constant stirring at room temperature (23 ± 1 °C), or higher (55 °C). After the experiment, as well as during the reaction, samples of the 'post' reaction mixtures were injected into a capillary column gas chromatograph for analysis. Standards were used to confirm the identification of the

product and prepare curves for the quantification of the product grade. Biphenyl (5 mM) was used as an internal standard. All experiments were performed three times, and the collected concentration values are the means of 3 independent experiments.

The controlled-potential bulk electrolysis experiments were performed with a potentiostat (Princeton Applied Research Model 273 A) using a 10 ml cell. The working electrode was a glassy carbon plate (area, 3 cm²), the auxiliary electrode was a platinum mesh, and the same reference electrode as described above was used (Ag/AgCl). Electrolysis was carried out with a constant potential equal to -0.3 V by 2 h at 23 ± 1 °C.

Thermodynamic calculations were made in Gaussian 16 [79] using DFT methods with the hybrid density functional B3LYP and the basis set def2-SVP. The structures were modeled by the GaussView program. Geometry optimization was conducted with the B3LYP/Def2SVP method with the added D3 version of Grimme's dispersion with Becke–Johnson damping [80,81]. The final electronic energies of the stationary points were calculated using the Def2-TZVP basis set with the added D3 version of Grimme's dispersion with Becke–Johnson damping and the PCM model of acetonitrile. Reported values combine these electronic energies with the ZPE correction or Gibbs free energy correction. The most stable form of the calculated catalyst structure was used to calculate the Gibbs free energy of the analyzed reactions.

4. Conclusions

 $[(salen)Fe^{II}]_{MeCN}$ is rapidly and completely oxidized by dioxygen to give the Fe(III) complex. The electrochemical reduction of $[(salen)Fe^{III}]_{MeCN}^+$ indicates that the catalytic process occurs and reactive oxygen species are formed during that process. Such an example of catalytic currents that arise from the oxidation of metal ions by molecular oxygen has not been previously described in the literature. The results presented demonstrate that the $[(salen)Fe^{III}]_{MeCN}^+$ complex is useful as a catalyst in the oxidation of cyclohexene by dioxygen ($p_{O2} = 0.2$ atm). As the main products, ketone and alcohol are formed and only tiny amounts of epoxide were found. Based on the results of the experiments conducted, a mechanism for the oxidation of $c-C_6H_{10}$ was proposed. The price and availability of the system of $[(salen)Fe^{III}]_{MeCN}^+$ activated by air ($p_{O2} = 0.2$ atm) are unquestionable advantages. These catalysts open up new perspectives for potential applications as key elements in the industry for the selective oxidation of organic compounds. However, knowledge of the reaction mechanism can contribute to a better understanding of the action of enzymes and dioxygen toxicity in living organisms.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/catal11121462/s1, Table S1: Oxidation of 1 M cyclohexene by air in acetonitrile at room temperature (23 ± 1 °C) catalyzed by the iron–salen complex at various concentrations. Reaction time 24 h, Figure S1: Dependence of product concentration for (1) ketone, (2) alcohol, (3) epoxide on time during oxidation of 1 M cyclohexene by air ($p_{O2} = 0.2$ atm) catalyzed by 1 mM [(salen)Fe^{II}]_{MeCN} in acetonitrile, room temperature 23 \pm 1 °C, Table S2: Concentrations of products for the oxidation of 1 M cyclohexene with dioxygen in acetonitrile catalyzed by different Fe-salen complexes (1 mM) after 24 h at room temperature (23 ± 1 °C), Figure S2: Cyclic voltammograms in acetonitrile ($0.1 \text{ M Et}_4\text{NClO}_4$) for 5 mM [(salen)Fe^{III}]⁺_{MeCN} in an air atmosphere. Scan rate, 0.1 Vs⁻¹, GCE (0.008 cm²); SCE vs. NHE, +0.242 V, cathodic scans, Figure S3: Cyclic voltammograms in acetonitrile (0.1 M Et₄NClO₄) for 5 mM [(salen)Fe^{III}](ClO₄) MeCN in (a) argon atmosphere, (b) air atmosphere, and after oxygen removal from previously oxygenated catalyst solution after (c) 5 min, (d) 10 min, and (e) 15 min of purging with Ar. Scan rate, 0.1 Vs⁻¹, GCE (0.008 cm²); SCE vs. NHE, +0.242 V, cathodic scans, Figure S4: Cyclic voltammograms in acetonitrile (0.1 M Et₄NClO₄) for 5 mM [(salen)Fe^{III}]Cl_{MeCN} in (a) argon atmosphere, (b) air atmosphere, and after deoxidation of previously oxygenated catalyst solution after (c) 5 min of deoxidation by use of Ar atmosphere. Scan rate, 0.1 Vs^{-1} , GCE (0.008 cm²); SCE vs. NHE, +0.242 V, cathodic scans, Figure S5: Cyclic voltammograms in acetonitrile (0.1 M Et₄NClO₄) for 5 mM [(salen)Fe^{II}]_{MeCN} in (a) argon atmosphere, (b) air atmosphere, and after oxygen removal of previously oxygenated catalyst solution after (c) 5 min, (d) 10 min, (e) 15 min, and (f) 45 min of purging with Ar. Scan rate, 0.1 Vs⁻¹, GCE (0.008 cm²); SCE vs. NHE, +0.242 V, cathodic scans, Figure S6: Cyclic

voltammograms in acetonitrile (0.1 M Et₄NClO₄) for iron species formed in a reaction of 1 mM $[(salen)Fe^{II}]_{MeCN}$ with O₂ and 1 M cyclohexene. (a) Air ($p_{O2} = 0.2$ atm) atmosphere, (b) dioxygen $(p_{O2} = 1 \text{ atm})$ atmosphere. Scan rate, 0.1 Vs^{-1} , GCE (0.008 cm²); SCE vs. NHE, +0.242 V, cathodic scans. Oxygenated catalyst with 1 M of cyclohexene in time after: I-0 min (immediately after aeration), II-30 min, III—3 h, IV—12 h, Figure S7: Dependence of $i (\mu A)$ on $\nu^{1/2} (mV/s)^{1/2}$ registered in acetonitrile (0.1 M Et₄NClO₄) for 1 mM [(salen)Fe^{II}]_{MeCN} in an argon atmosphere for (a) cathodic (-0.1 V) and (b) anodic (~0 V) peaks, Figure S8: Cyclic voltammograms in acetonitrile (0.1 M Et₄NClO₄) for 1 mM [(salen)Fe^{II}]_{MeCN} under Ar atmosphere (a) with 15 mM PhIO, (b) with 15 mM PhIO and 30 mM HClO₄. Scan rate, 0.1 Vs^{-1} , GCE (0.008 cm²); SCE vs. NHE, +0.242 V, cathodic scans, Table S3: Energies (with and without zero-point correction), enthalpies, free energies (G), and respective relative values for different catalyst molecules calculated with Def2SVP, Table S4: Energies (with and without zero-point correction), enthalpies, free energies (G) calculated with Def2TZVP, and the MeCN model for the best multiplicity of different catalyst molecules determined on the basis of the data presented in Tables S3 and S5: Relative energies and Gibbs free energies and values of ε_0 . ZPE, Ecorr, Hcorr, Gcorr of the singlet (1), triplet (3), and quintet (5) for the reaction of cyclohexene oxidation catalyzed by [(salen)Fe^{IV}=O] to alcohol and [(salen)Fe^{II}]. Calculated relative energies with ZPE correction as well as Gibbs free energies are given in reference to substrate ³S, Figure S9: Relative Gibbs free enthalpies (Table S5) of the singlet (1, gray), triplet (3, black), and quintet (5, green) for the reaction of cyclohexene oxidation catalyzed by [(salen)Fe^{IV}=O] to alcohol. For the initial complexes S (in three various spin states) the values of starting relatives Gibbs free enthalpies are given next to the respective line. The legend of used symbols: S-substrates: [(salen)Fe=O)]+H-C₆H₉, TSI-[(salen)Fe-O-H-C₆H₉], PI-products1: [(salen)Fe-OH)]+C₆H₉, TSII-[(salen)Fe-O(H)-C₆H₉], PII-products2: [(salen)Fe]+C₆H₉OH.

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