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Catalytic and Stoichiometric Baeyer–Villiger Oxidation Mediated by Nonheme Peroxo-Diiron(III), Acylperoxo, and Iodosylbenzene Iron(III) Intermediates

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Abstract: In this paper we describe a detailed mechanistic studies on the [Fe^{II}(PBO)_{2}(CF_{3}SO_3)]_{2} (I), [Fe^{II}(PBT)_{2}(CF_{3}SO_3)]_{2} (2), and [Fe^{II}(PBI)_{2}(CF_{3}SO_3)]_{2} (3)-catalyzed (PBO = 2-(2'-pyridyl)benzoxazole, PBT = 2-(2'-pyridyl)benzthiazole, PBI = 2-(2'-pyridyl)benzimidazole) Baeyer–Villiger oxidation of cycloketones by dioxygen with cooxidation of aldehydes and peroxycarboxylic acids, including the kinetics on the reactivity of (μ-1,2-peroxo)diiron(III), acylperoxo- and iodosylbenzene-iron(III) species as key intermediates.

Keywords: Baeyer–Villiger oxidation; peroxo-diiron(III); oxoiron(IV); catalysis; kinetic studies

1. Introduction
Baeyer–Villiger oxidation has become one of the most important reactions in organic chemistry with a large range of possible applications because the forming lactones or esters are important industrial intermediates in the synthesis of various pharmaceuticals, monomers for polymerization, pheromones, and herbicides for agrochemistry. These reactions have been commonly carried out by the use of expensive, shock-sensitive, and potentially explosive peroxycarboxylic acids as oxidants [1–4]. Peracids (iminoperacids) can be efficiently generated in situ from nitriles (solvent) and H_{2}O_{2} in the presence of solid bases or from aldehydes and dioxygen in the presence of metal compounds [5–17]. This way, the major disadvantages, namely handling large amounts of peracid, and the noncatalytic use of acid, can be avoided. A combination of molecular oxygen and aldehydes under homogeneous and heterogeneous catalysis has also been extensively studied. Baeyer–Villiger oxidation of cyclic ketones to lactones catalyzed by silica-supported nickel complex, iron(III)-containing mesoporous silica, and Mg-Al hydrotalcites has been reported [18–24]. In the homogeneous phase, efficient selective oxidation of cyclohexanones to lactones by molecular oxygen with benzoaldehyde as an oxygen acceptor, in the presence of Fe(TPP)Cl, Ru(TPP)Cl, Co(TPP)Cl and Mn(TPP)Cl (TPP—meso-tetraphenylporphyrin) complexes, has been reported [25,26]. In the benzoaldehyde-mediated aerobic Baeyer–Villiger oxidation of the cyclohexanone system, high-valent iron porphyrin was the oxidative species to produce 3-caprolactone [26]. Type III Baeyer–Villiger monooxygenases (BVMOs [27–33]) are specific cytochrome P450s, which are involved in the synthesis of brassinosteroids—steroidal hormones essential for the growth and development of plants [27]. Iron complexes of meso-tetraphenylporphyrin, Fe^{III}(TPP)Cl [25,26], and N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)ethyliron(II) complex, Fe^{II}(N4P)/CH_{3}CN^{2+}, have been proposed as key intermediates for the aerobic oxidation of cyclohexanone in the presence of various aldehydes as sacrificial reductants, wherein, contrary to the heme-containing monooxygenases, a high-valent iron porphyrin, Fe^{V}(TPP)(O)Cl and Fe^{IV}(N4P)(O)(O)^{2+} were proposed as key intermediates in the rate-determining oxygen atom transfer step to generate the ε-caprolactone [34]. Oxidation of...
four substituted cyclohexanone derivatives by oxoiron(IV) complex, [FeIV(asN4Py)(O)]2+ with chiral pentadentate ligand, N,N-bis(2-pyridylmethyl)-1,2-di(2-pyridyl)ethylamine, attained moderate enantioselectivities up to 45% enantiomeric excess (ee) [35]. In the literature, only a few examples can be found where the peroxo-diiron(III) species is capable of direct nucleophilic reactions, such as oxidative dehydroxylation of aldehydes and Baeyer–Villiger oxidation of cyclohexanones [36–39]. The coordination chemistry of nitrogen-rich nonsymmetric bidentate ligands has received much attention. We have demonstrated that by tuning the ligands d-donor/π-acceptor strength, the reactivity and the formation rate of intermediate (μ-1,2-peroxo)diiron(III) complexes in the reaction of their iron(II) precursor complexes with H2O2 can be influenced [38]. Here we report the formation of (μ-1,2-peroxo)diiron(III), FeIII(mCPBA), and FeIII(OIPh) complexes by the use of various oxidants such as H2O2, m-chloroperoxybenzoic acid (mCPBA), iodosylbenzene (PhIO), and benzaldehyde with O2, and their nucleophilic reactivity in stoichiometric and catalytic Baeyer–Villiger oxidation reactions (Scheme 1).

Scheme 1. Iron(II) complexes with bidentate ligands were used as Baeyer–Villiger catalysts.

2. Results and Discussion

We have previously reported the synthesis and structure of [FeII(PBO)2(CF3SO3)2] (1), [FeII(PBT)2(CF3SO3)2] (2), and [FeII(PBI)3](CF3SO3)2 (3) (PBO = 2-(2'-pyridyl)benzoxazole, PBT = 2-(2'-pyridyl)benzothiazole, PBI = 2-(2'-pyridyl)benzimidazole) complexes, and spectroscopic characterization of their transient green species with a FeIII(μ-1,2-O2)FeIII core (λmax = 685–720 nm, and ε ~1400) as a result of the reaction of 1–3 with H2O2 [40]. Based on detailed kinetic and computational studies, we have found direct evidence for the formation of low-spin oxoiron(IV) species in a pre-equilibrium process during the oxidation of phenols as ribonucleotide reductase (RNR-R2) models [41]. We have also published the iron(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone, where similarly to the previously published FeIII(TPP)Cl [25,26] system, oxoiron(IV) intermediate was suggested as a reactive intermediate during the oxygen transfer step. Since the two intermediates above have different characteristics (electrophilic versus nucleophilic for FeIVO and FeIII(μ-1,2-O2)FeIII, respectively), the question arises as to which form can be used to interpret the mechanism in the case of our selected complexes (1–3). Since the mechanism of the Baeyer–Villiger reaction can be interpreted essentially through a nucleophilic addition (AN) step, the peroxo-diiron intermediate may be a suitable candidate. Our primary goal is to elucidate the role of the two possible intermediates in the catalytic and stoichiometric oxidation reaction of cycloketones.

2.1. Catalytic Tests for the Iron(II)-Catalyzed Baeyer–Villiger Oxidation of Cycloketones

As a first step, the catalytic activity of complexes 1–3 was investigated using the conditions described in the literature for the FeIII(TPP)Cl-containing catalytic system [25,26].
Reactions were carried out in toluene at 60 °C under air, where catalyst, substrate, and aldehyde were in a molar ratio of 1:1000:15,000, respectively (Table 1 and Figure 1). In this system, peracids can be efficiently generated in situ from aldehydes and dioxygen in the presence of metal compounds, which act as the active oxygen species in the B–V reaction. The consumption of the cyclohexanone and the formation of the ε-caprolactone were monitored by GC and GC-MS. There was, remarkably, a difference in efficiency between the three kinds of catalysts (1–3) compared with the previously investigated FeIII(TPP)Cl complex. Figure 1 shows the profiles of cyclohexanone aerobic oxidation catalyzed by PBO, PBT, and PBI complexes with benzaldehyde as coreductant, compared with the previously reported metalloporphyrin-catalyzed B–V oxidation system. The conversion of cyclohexanone in all cases increased rapidly within the first 1 h period (Figure 1a), and the conversion reached 48%, 72.8%, and 85% after 5 h for 3, 2, and 1, respectively. The relative reactivity of catalysts is in the following order 1 > 2 > 3 (Figure 1a). The obtained reactivity order can be explained by the different structures of the complexes and the effect of the ligand framework. Much higher reactivity was observed for the coordinative unsaturated bisz FeIII(PBO) (1) and FeIII(PBT)2 (2) complexes. Furthermore, the electrochemical properties of the complexes show significant differences, which may also explain the different reactivity. Complex 3 exhibit a quasi-reversible redox couple at 0.90 V vs. Ag/AgCl (Epa(FeIII/II) = +0.94 V and Epc(FeIII/II) = +0.85 V). The irreversible reductions at potentials more negative than −1.0 V are assigned to ligand-centred one-electron reductions. The FeIII/FeII redox couples of 1 (Epa(FeIII/II) = +1.55 V and Epc(FeIII/II) = +0.42 V) and 2 (Epa(FeIII/II) = +1.44 V and Epc(FeIII/II) = +0.32 V) are both irreversible and are considerably higher potentials than for 3, consistent with the electron-withdrawing nature of O and S compared with NH [40].

Table 1. Comparison of the efficiency for the iron(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone by molecular oxygen in the presence of benzaldehyde 1.

| Catalyst                  | Time (h) | Conversion (%) | TOF (h−1) 2 |
|---------------------------|----------|----------------|-------------|
| [Fe(PBO)(OTf)2] (1)       | 0.5      | 28.90          | 578.0       |
| [Fe(PBO)(OTf)2] (1)       | 1        | 55.90          | 599.0       |
| [Fe(PBO)(OTf)2] (1)       | 2        | 81.70          | 408.5       |
| [Fe(PBO)(OTf)2] (1)       | 5        | 85.00          | 170.0       |
| [Fe(PBT)(OTf)2] (2)       | 0.5      | 40.65          | 813.0       |
| [Fe(PBT)(OTf)2] (2)       | 1        | 59.45          | 594.5       |
| [Fe(PBT)(OTf)2] (2)       | 2        | 71.35          | 356.8       |
| [Fe(PBT)(OTf)2] (2)       | 5        | 72.80          | 145.0       |
| [Fe(PBI)(OTf)2] (3)       | 0.5      | 10.07          | 201.4       |
| [Fe(PBI)(OTf)2] (3)       | 1        | 32.33          | 323.3       |
| [Fe(PBI)(OTf)2] (3)       | 2        | 42.31          | 211.5       |
| [Fe(PBI)(OTf)2] (3)       | 5        | 47.67          | 95.0        |

1 [Fe] (0.01 mM), cyclohexanone (10 mM), benzaldehyde (150 mM), toluene (5 mL), O2 bubbling, 60 °C, 5 h.
2 TOF—Turnover per hour.

It can be seen that the conversions increases with time in all cases (Table 1). However, catalyst efficiency (turnover frequency (TOF) = the number of turnovers/h) decreased with time, indicating that with longer reaction times, catalytic efficiency could be lost.

Since the solvent can play a role in the stabilization of polar intermediates during the reaction pathway, in this sense, acetonitrile with a higher polarity was chosen as the solvent. Based on our previous experience, the most common solvent for the preparation of oxoiron(IV) and peroxo-diiron(II) intermediates is acetonitrile. Table 2 and Figure 2 present the preliminary kinetic results of the cyclohexanone oxidation catalyzed by 2 with benzaldehyde under oxygen, including the values of conversions and the number of turnovers. The conversion of cyclohexanone is 28% without catalyst but occurs with much higher yields in the presence of 2 compared with the classical Baeyer–Villiger reaction. The effect of the complex concentration was investigated under fixed conditions (Table 2, entries 1–5, and Figure 2a) at 60 °C. High selectivity was achieved in all runs, and maximum
Conversions were obtained in the range of 0.01–0.10 × 10⁻⁵ M complex (2) concentration. It means that complex 2 proved to be an efficient catalyst for cyclohexanone oxidation. Further increase in the concentration of the complex results in a decrease in conversion, which can be explained by the oxidation of benzaldehyde as a competing substrate and the formation of a catalytically inactive μ-oxo-diiron(III) complex. However, in the O₂/aldehyde oxidation system, large amounts of aldehydes were required as sacrificing agents for the oxidation of cyclohexanone to obtain high conversion values (Table 2, entries 6–10, Figure 2b).

![Figure 1](image1.jpg)

**Figure 1.** Comparison of the efficiency for the oxidation of cyclohexanone employing [Fe^{III}(PBO)(CF₃SO₃)₂] (1), [Fe^{III}(PBT)(CF₃SO₃)₂] (2), and [Fe^{III}(PBI)(CF₃SO₃)₂] (3) as catalysts: (a) time course of the oxidation of cyclohexanone; (b) comparison of the efficiency based on yields. Reaction conditions: [Fe] (0.01 mM), cyclohexanone (10 mM), benzaldehyde (150 mM), toluene (5 mL), O₂ bubbling, 60 °C, 5 h.

**Table 2.** Dependence between the conversion and number of turnover values on the catalyst (2) and benzaldehyde concentrations for the iron(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone by molecular oxygen in the presence of benzaldehyde ¹.

| Entry | Catalyst (10⁻² mM) | Benzaldehyde (mM) | Conversion (%) | TOF (h⁻¹) ² |
|-------|-------------------|------------------|---------------|------------|
| 1     | 0.01              | 150              | ~100          | 4800       |
| 2     | 0.05              | 150              | ~100          | 960        |
| 3     | 0.1               | 150              | ~100          | 480        |
| 4     | 0.2               | 150              | 95            | 223        |
| 5     | 0.6               | 150              | 83            | 61         |
| 6     | 1.0               | 150              | 81            | 35         |
| 7     | 1.0               | 25               | 33            | -          |
| 8     | 1.0               | 50               | 42            | -          |
| 9     | 1.0               | 100              | 60            | -          |
| 10    | 1.0               | 175              | 87            | -          |

¹ [2] (0.01–1.0 × 10⁻⁵ M), cyclohexanone (10 mM), benzaldehyde (25–175 mM), CH₂CN (5 mL), O₂ bubbling, 60 °C, 15 h. ² Normalized with the stoichiometric result (Conversion = 28% without catalyst).

Competitive reactions were also performed with parasubstituted benzaldehyde derivatives in order to evaluate the influence of electronic factors on the metal-free and metal-based reactions (Figure S1). Relative reactivities have shown linear correlations with Hammett’s σ constants. The negative reaction constants ρ were negative (ρ = −0.46 for 2 and −0.68 for BA/O₂), suggesting that the rate-determining steps are nucleophilic in both cases.

The scope of substrates for the Baeyer–Villiger oxidation catalyzed by the [Fe(PBT)(OTf)₂] (2) was examined, and the typical results are shown in Table 3. In general, the more electron-rich (most-substituted) alkyl group migrates in preference but based on the calculated TOF values (~34), no significant effect has been observed for the alkyl substitution except for 4⁴Bu-cyclohexanone and 3-Me-cyclohexanone, probably because of a solubility problem.
and more sensitive steric 1,3-interactions, respectively (Figure 3, Table 3, entries 3 and 4). The same trend has been observed for the metal-free system indicating a similar mechanism.

Figure 2. Preliminary kinetic study on the iron(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone by molecular oxygen in the presence of benzaldehyde. (a) Plot of conversion versus catalyst (2) concentration; (b) Plot of conversion versus benzaldehyde concentration reaction conditions: [2] (0.01–1.0 × 10^{-2} mM), cyclohexanone (10 mM), benzaldehyde (25–175 mM), CH3CN (5 mL), O2 bubbling, 60 °C, 15 h.

Table 3. Oxidation of various ketones by dioxygen in the presence and absence of [Fe(PBT)(OTf)2] (2) 1.

| Entry | Ketones | Product | Conversion (%) | Yield (%) | TOF (h^{-1}) |
|-------|---------|---------|---------------|-----------|--------------|
| 1     |        |         | 81 (28) 2     | 81 (28) 2 | 35           |
| 2     |        |         | 77 (25.5) 2   | 77 (25.5) 2 | 34           |
| 3     |        |         | 23 (2) 2,3    | 23 (2) 2  | 14           |
| 4     |        |         | 70 (18.5) 2   | 70 (18.5) 2 | 34           |
| 5     |        |         | 30 (4) 2      | 30 (4) 2  | 17           |

1 [Fe(PBT)(OTf)2] (2) (0.01 mM), cyclohexanone (10 mM), benzaldehyde (150 mM), CH3CN (5 mL), O2 bubbling, 60 °C, 15 h. 2 Normalized with the stoichiometric results (without catalyst). 3 Two products were formed in a 1:1 ratio.

Since the proposed oxidant is the peroxycbenzoic acid (PBA) in the BA/O2 system studied above, we have also investigated the Baeyer–Villiger oxidation of cyclohexanone by the use of mCPBA as the oxidant. Figure 4 and Table 4 show the catalytic activity of the
three catalysts (1–3). Among the catalysts tested, similarly to the BA/O₂ systems, 2 and 3 showed the highest activity with ~70% conversion and ~100 turnover per hour.

![Comparison of the efficiency for the iron(II)-catalyzed oxidation of cyclohexanone employing Fe(PBO)(OTf)₂ (1), Fe(PBT)(OTf)₂ (2), and Fe(PBI)(OTf)₂ (3) as catalysts. Reaction conditions: [Fe] (0.01 mM), cyclohexanone (10 mM), benzaldehyde (150 mM), CH₃CN (5 mL), O₂ bubbling, 60 °C, 15 h.](image)

**Figure 3.** Yields without and with a catalyst for the 2-catalyzed *Baeyer–Villiger* oxidation of cyclohexanones. Reaction conditions: [Fe(PBT)(OTf)₂] (2) (0.01 mM), cyclohexanone (10 mM), benzaldehyde (150 mM), CH₃CN (5 mL), O₂ bubbling, 60 °C, 15 h.

**Figure 4.** Comparison of the efficiency for the oxidation of cyclohexanone employing [Fe³⁺(PBO)₂(CF₃SO₃)₂] (1), [Fe³⁺(PBT)₂(CF₃SO₃)₂] (2), and [Fe³⁺(PBI)₃](CF₃SO₃)₂ (3) as catalysts. Reaction conditions: [Fe] (0.01 mM), cyclohexanone (10 mM), mCPBA (150 mM), CH₃CN (5 mL), 60 °C, 5 h.

**Table 4.** Comparison of the efficiency for the iron(II)-catalyzed *Baeyer–Villiger* oxidation of cyclohexanone with mCPBA ¹.

| Catalyst | Time (h) | Conversion (%) | TOF (h⁻¹) ² |
|----------|----------|----------------|-------------|
| [Fe(PBO)(OTf)₂] (1) | 5 | 70.4 | 107 |
| [Fe(PBT)(OTf)₂] (2) | 5 | 67.3 | 101 |
| [Fe(PBI)(OTf)₂] (3) | 5 | 54.8 | 76 |
| - | 5 | 16.8 | - |

¹ [Fe] (0.01 mM), cyclohexanone (10 mM), mCPBA (150 mM), CH₃CN (5 mL), 60 °C, 5 h. ² Normalized with the stoichiometric results (without catalyst).
The conversion of the cyclohexanone into ε-caprolactone can be significantly increased by increasing the amount of catalyst, and the highest conversion value (67%) was observed in a molar ratio of 1 (2):1000 (Substrate):15,000 (mCPBA) (Figure 5a and Table 5, entries 1–5). A similar ratio (1:1000:15,000) and conversion value (78%) were observed when the effect of oxidant was investigated (Figure 5b and Table 5, entries 6–9).

Figure 5. Preliminary kinetic study on the iron(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone by mCPBA. (a) Plot of conversion versus catalyst (2) concentration; (b) Plot of conversion versus mCPBA concentration Reaction conditions: [2] (0.01–1.0 × 10⁻⁷ M), cyclohexanone (10 mM), benzaldehyde (25–175 mM), CH₃CN (5 mL), 60 °C, 5 h.

Table 5. Dependence between the conversion and number of turnover values on the catalyst (2) and mCPBA concentrations for the iron(II)-catalyzed Baeyer–Villiger oxidation of cyclohexanone by mCPBA ¹.

| Entry | Catalyst (10⁻⁴ mM) | mCPBA (mM) | Conversion (%) |
|-------|-------------------|------------|---------------|
| 1     | 0.01              | 150        | 27            |
| 2     | 0.1               | 150        | 50            |
| 3     | 1.0               | 150        | 62            |
| 4     | 10                | 150        | 65            |
| 5     | 100               | 150        | 67            |
| 6     | 10                | 25         | 15            |
| 7     | 10                | 50         | 26            |
| 8     | 10                | 100        | 52            |
| 9     | 10                | 175        | 78            |

¹ [2] (0.01–100) × 10⁻⁷ M), cyclohexanone (10 mM), mCPBA (25–175 mM), CH₃CN (5 mL), 60 °C, 5 h.

2.2. Stoichiometric Peroxo-Diiron(III)-Mediated Baeyer–Villiger Oxidation of Cycloketones

To get more insight into the mechanism of the catalytic reactions above, it was important to study the formation of possible intermediates by the use of various oxidants and investigate their stoichiometric oxidation with cycloketones. We have found earlier that the addition of H₂O₂ to acetonitrile solutions of the [Fe³⁺(PBI)₃](CF₃SO₃)₂ (3) results in the rapid colour from red to green (λmax = 720 nm, ε = 1360 M⁻¹·cm⁻¹), which can be ascribed to the charge transfer between Fe(III) and the O₂²⁻ ligand [40,41]. Complex (3) can also be easily oxidized with mCPBA (Figure 6a), PhIO (Figure 7a), and BA under air (Figure 8a), resulting in a characteristic shift of the NIR absorption band in λmax to 760 nm (ε= 1400 M⁻¹·cm⁻¹). The half-lives (t½’s) for complex 3PhIO is 7200 s at 15 °C. Based on the UV–Vis spectra, intermediates 3PhIO, 3mCPBA, and 3BA show a high degree of similarity to species 3H₂O₂. These results may suggest the formation of metastable peroxodiiron(III) species in all cases.
These results suggest a high similarity between S = ½ low-spin monomeric iron(III) species (Fe\textsuperscript{III}(mCPBA) and Fe\textsuperscript{III}(OIPh)) (Figure S3). S = ½ low-spin monomeric iron(III) species (Fe\textsuperscript{III}(mCPBA) and Fe\textsuperscript{III}(OIPh)) (Figure S3).

Assignment of the EPR features of 3\textsuperscript{mCPBA} with PhIO. Conditions [3] = 1 mM in MeCN at 5 °C, \(\lambda = 760\) nm.

A solution of 3 in MeCN was titrated with mCPBA dissolved in MeCN. Aliquots of mCPBA were added to the solution of 3, and the UV–Vis spectral changes were recorded after each addition (Figure 6b). Correction for dilution was applied. Spectral changes at 760 nm were plotted against the added mCPBA. Almost the same species could be observed with complexes 1 and 2 but in much lower yields (\(-10\%\) based on 3\textsuperscript{PhIO} at 5 °C), which can be explained by the much lower thermal stability of the forming intermediates caused by the two available coordination sites in the precursor bis-complexes.

Similarly, a MeCN solution of 3 was subjected to titration with PhIO dissolved in \(\text{CH}_2\text{Cl}_2\) (Figure 7b). Complex 3 reacts rapidly with mCPBA or PhIO at room temperature to afford 3\textsuperscript{mCPBA}, which is almost identical to 3\textsuperscript{PhIO}, as confirmed by UV–Vis. Consistent with the 3\textsuperscript{mCPBA} titration of 3 with m-CPBA, monitored by UV–Vis spectroscopy, requires one equivalent of mCPBA. Similar changes are observed during the titration of 3 with PhIO. These results suggest a high similarity between 3\textsuperscript{mCPBA} and 3\textsuperscript{PhIO} species.
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However, the resulting species decomposes rapidly, which can be explained by its reaction with benzaldehyde. The second-order rate constant in the oxidation of benzaldehyde with $3\text{BAO}_2$ is 1.4 M$^{-1}$s$^{-1}$ at 298 K, which is twice less than that observed for complexes $3\text{H}_2\text{O}_2$ (2.39 M$^{-1}$s$^{-1}$ at 288 K). The small difference in reaction rates may be explained by the different nature of the intermediates ($3\text{H}_2\text{O}_2$ and $3\text{BAO}_2$) formed.

The Hammett plot analysis shows that the rate constant for the oxidation of benzaldehyde by the in situ-forming $3\text{BAO}_2$ is sensitive to changes in the electronic properties of the benzaldehyde, with a $\rho$ value of +0.43, suggesting a nucleophilic attack of the proposed peroxide on the aldehyde C-atom in the rate-determining step (8b). This result is consistent with that obtained for the two catalysed oxidation of cyclohexanone using parasubstituted

Figure 8. Spectral changes during the reaction of 3 with benzaldehyde under air: (a) UV–Vis absorption spectra of complex 3 after the addition of 15 equivalents of benzaldehyde under air. Conditions: $[3] = 1$ mM, $[\text{BA}] = 15$ mM, $\lambda = 760$ nm. (b) Hammett plot for the reaction of the in situ formed $3\text{BAO}_2$ intermediate with the excess of benzaldehyde derivatives. Conditions $[3] = 1$ mM, $[4\text{R-BA}, \text{R} = \text{Me, H, Cl, and CN}] = 20$ mM in MeCN at 5 °C.

We have previously reported that the rR spectroscopy at $\lambda_{\text{exc}}$ 785 nm shows enhancement of bands at 876 and 463 cm$^{-1}$ that are typical of a Fe(III)-O-O-Fe(III) core upon addition of $\text{H}_2\text{O}_2$ to the solution of 3 [40]. The correspondence of the observed and calculated shifts in the bands at 876 cm$^{-1}$ (to 826) and 463 cm$^{-1}$ (to 445 cm$^{-1}$) where $\text{H}_2\text{O}_2$ was employed supported the assignment of bands as the O-O and Fe-Fe stretching modes, respectively. Despite the similarity of the UV–Vis spectra, the formation of peroxy-diiron(III) species can be ruled out in the case of $3\text{mCPBA}$ and $3\text{PhIO}$ intermediates, based on their rRaman spectra (Figure S2). In the case of PhIO, the bands at 462 and 900 cm$^{-1}$, which seem promising, are unfortunately not $^{18}$O sensitive, and the same species is formed regardless of oxidation. They are probably derived from PhI. Contrary to the EPR spectrum of $3\text{H}_2\text{O}_2$, which shows only trace levels of mononuclear high and low-spin iron complexes, the EPR signals of $3\text{PhIO}$ and $3\text{mCPBA}$ ($g = -2.29$ and $-1.87$) can be assigned to the S = $\frac{1}{2}$ low-spin monomeric iron(III) species (Fe$^{\text{III}}$(mCPBA) and Fe$^{\text{III}}$(OIPh)) (Figure S3). Assignment of the EPR features of $3\text{mCPBA}$ to a low spin 3-chloroperoxybenzoatoiron(III) complex is consistent with similar EPR features observed for other S = $\frac{1}{2}$ low-spin acylperoxoiron(III) complexes [42].

Similar changes are observed during the titration of 3 with PhIO. These results suggest the formation of metastable peroxydiiron(III) species in both cases.

Figure 8a shows the formation of the in situ formed $3\text{PBA}$ species in the reaction of 3 with an excess of benzaldehyde under air at 5 °C in CH$_3$CN. The same species can be observed by the use of parasubstituted benzaldehydes under identical conditions. However, the resulting species decomposes rapidly, which can be explained by its reaction with excess benzaldehyde. The second-order rate constant in the oxidation of benzaldehyde by $3\text{PBA}$ is 1.4 M$^{-1}$s$^{-1}$ at 298 K, which is twice less than that observed for complexes $3\text{H}_2\text{O}_2$ (2.39 M$^{-1}$s$^{-1}$ at 288 K). The small difference in reaction rates may be explained by the different nature of the intermediates ($3\text{H}_2\text{O}_2$ and $3\text{PBA}$) formed.

The Hammett plot analysis shows that the rate constant for the oxidation of benzaldehyde by $3\text{PBA}$ is sensitive to changes in the electronic properties of the benzaldehyde, with a $\rho$ value of +0.43, suggesting a nucleophilic attack of the proposed peroxide on the aldehyde C-atom in the rate-determining step (8b). This result is consistent with that obtained for the two catalysed oxidation of cyclohexanone using parasubstituted
benzaldehydes (Figure S1). Similar values were obtained for (μ-1,2-peroxo)diiron(III) complexes with Me-PBI (+0.67), and (μ-oxo)(μ-1,2-peroxo)diiron(III) complex with indH (+0.48) ligands [36–39].

To get direct evidence for the involvement of a $^{3}$PhIO species in the Baeyer–Villiger oxidation, the reaction of $^{3}$PhIO with various cycloketone derivatives was investigated. The $^{3}$PhIO complex was generated by the reaction of 3 with PhIO, and the rate of the decay of the absorption band at 760 nm with cyclohexanone was measured as a function of the concentration of added cyclohexanone derivatives (Figure 9a). It was found that the $^{3}$PhIO species is able to oxidize the cyclohexanone derivatives to the corresponding ε-caprolactones. The relative reactivity of substrates is in the following order: 4′Bu-cyclohexanone > cyclohexanone > 2Me-cyclohexanone > 3Me-cyclohexanone > 4Me-cyclohexanone (Figure 9a and Table 6). The oxidation of other cyclic ketones, such as cyclopentanone and cyclobutanone, was also examined (Figure 9b and Table 6). Their relative reactivity shows the following order: cyclohexanone > cyclopentanone > cyclobutanone, and correlates very well with their endocyclic bond angles (Figure 10). Since no reaction has been observed for benzophenone, this indicates clearly that the conjugation of the carbonyl group decreases the reactivity of the ketone.

**Table 6. Reaction rates determined in the reactions of 3PhIO with various cyclohexanone derivatives.**

| Substrate | $k_{\text{obs}}$ (×10$^{-3}$ s$^{-1}$) |
|-----------|-------------------------------------|
| Cyclohexanone | 7.17 ± 0.18 |
| 2-Methylcyclohexanone | 1.48 ± 0.05 |
| 3-Methylcyclohexanone | 0.71 ± 0.02 |
| 4-Methylcyclohexanone | 9.21 ± 0.40 |

**Figure 9.** Stoichiometric Baeyer–Villiger oxidation of cycloketone derivatives: (a) Absorbance change at 760 nm versus time in the $^{3}$PhIO-mediated oxidation of cyclohexanones: without substrate (a), 4′-tert-Butylcyclohexanone (b), 3-Methylcyclohexanone (c), 2-Methylcyclohexanone (d), Cyclohexanone (e), 4-Methylcyclohexanone (f). Reaction conditions: $[3] = 10^{-3}$ M, [sub.]= 0.35 M, at 15 °C; (b) Absorbance change at 760 nm versus time in the $^{3}$PhIO-mediated oxidation of cycloketones: without substrate (a), cyclobutanone (b), cyclopentanone (c), cyclohexanone (d). Reaction conditions: $[1] = 10^{-3}$ M, [sub.] = 0.35 M, T = 15 °C, the intermediate was generated with PhIO in MeCN.

The traces could be fitted with a first-order kinetic law, with respect to $^{3}$PhIO, and the calculated $k_{\text{ox}}$ values (-d $[^{3}$PhIO]/dt = $k_{\text{obs}}$[$^{3}$PhIO] = ($k_{0} + k_{\text{ox}}$[S])[$^{3}$PhIO]), for different concentrations of the appropriate substrate are reported in Table 7. Kinetic experiments revealed first-order dependence on both the substrate (cyclohexanone) (Figure 11) and the $^{3}$PhIO concentration (Figure 12a) with $k_{\text{s}} = 7.17 \times 10^{-2} \text{ M}^{-1} \text{s}^{-1}$, $\Delta H^\circ = 23 \pm 3 \text{ kJ mol}^{-1}$, and $\Delta S^\circ = -185 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1}$ at 15 °C (Figure 12b). This value is six times smaller than that measured for $^{3}$H$_{2}$O$_{2}$ (0.4 M$^{-1}$ s$^{-1}$) under the same conditions, which may also indicate a different structure of the two oxidants.
Table 6. Reaction rates determined in the reactions of $3^{\text{PhIO}}$ with various cycloketones in MeCN at 15 °C.

| Entry | Substrate                | $k_{\text{ox}}$ ($10^{-2} \text{ s}^{-1}$) | Yield (%) |
|-------|--------------------------|------------------------------------------|-----------|
| 1     | Cyclohexanone            | 7.17 ± 0.18                              | 60        |
| 2     | 2-Methylcyclohexanone    | 1.48 ± 0.05                              | 55        |
| 3     | 3-Methylcyclohexanone    | 0.71 ± 0.02                              | 53        |
| 4     | 4-tert-Butylcyclohexanone| 0.58 ± 0.02                              | 50        |
| 5     | Methylcyclohexanone      | 9.21 ± 0.40                              | 65        |
| 6     | Cyclopentanone           | 5.46 ± 0.21                              | 28        |
| 7     | Cyclobutanone            | 1.29 ± 0.03                              | 25        |

1 Based on 3.

Figure 10. Correlation between endocyclic bond angle (α) and the rate constant ($k_{\text{obs'}}$) for the decay of $3^{/\text{PhIO}}$ in the presence of cyclic ketones. Reaction conditions: [3] = $10^{-3}$ M, [sub.] = 0.35 M at 15 °C, $3^{\text{PhIO}}$ was generated with PhIO in MeCN.

Figure 11. Stoichiometric $3^{\text{PhIO}}$–mediated Baeyer–Villiger oxidation of cyclohexanone: (a) UV-Visible spectral change for $3^{\text{PhIO}}$–mediated oxidation of cyclohexanone in MeCN at 15 °C ($\Delta t = 10$ s). Inset: The change of $3^{\text{PhIO}}$ concentration derived from the reaction of $3^{\text{PhIO}}$ and cyclohexanone: [3] = $10^{-3}$ M, without substrate (a), [substrate] = 0.1 M (b) [substrate] = 0.15 M (c), [substrate] = 0.2 M (d); (b) Substrate dependence. [3] = $10^{-3}$ M, T = 15 °C, iron(III) intermediates ($3^{\text{PhIO}}$ and $3^{\text{H}_2\text{O}_2}$) were generated with PhIO and H$_2$O$_2$, respectively, the $k_{\text{obs'}}$ data were taken from the Table 1.
The formation of the peroxo species is fast, the rate-determining step is likely to occur through the iron(III) intermediate. Since the formation of the peroxo species is fast, the rate-determining step is likely to occur through the iron(III) intermediate. Based on our previous and current results, we have found no evidence for the formation of characteristic oxoiron(IV) species and their possible role in the oxidation of cyclohexanone via electrophilic OAT mechanism (Scheme 2C).

The change of 3-PhIO concentration derived from the reaction of H₂O₂, respectively, the formation of the peroxo species is fast, the rate-determining step is likely to occur through the iron(III) intermediate. Based on our previous and current results, we have found no evidence for the formation of characteristic oxoiron(IV) species and their possible role in the oxidation of cyclohexanone via electrophilic OAT mechanism (Scheme 2C).

Table 7. Kinetic data for the stoichiometric Baeyer–Villiger oxidation of cyclohexanone with 3-PhIO and 3H₂O₂.

| Entry | [J] (mM) | Cyclohexanone (mM) | T (K) | k_{obs'} (10^{-2} s^{-1}) | k_{ox} (10^{-2} M^{-1}s^{-1}) |
|-------|----------|-------------------|-------|--------------------------|-------------------------------|
| 1     | 0.5      | 350               | 288   | 2.67 ± 0.08              | 7.63 ± 0.22                  |
| 2     | 1.0      | 350               | 288   | 2.51 ± 0.07              | 7.17 ± 0.18                  |
| 3     | 1.5      | 350               | 288   | 2.58 ± 0.08              | 7.38 ± 0.23                  |
| 4     | 2.0      | 350               | 288   | 2.52 ± 0.07              | 7.19 ± 0.17                  |
| 5     | 1.0      | 100               | 288   | 0.72 ± 0.02              | 7.21 ± 0.18                  |
| 6     | 1.0      | 125               | 288   | 0.90 ± 0.02              | 7.21 ± 0.18                  |
| 7     | 1.0      | 150               | 288   | 1.10 ± 0.04              | 7.34 ± 0.25                  |
| 8     | 1.0      | 200               | 288   | 1.47 ± 0.06              | 7.35 ± 0.31                  |
| 9     | 1.0      | 350               | 288   | 2.51 ± 0.10              | 7.17 ± 0.29                  |
| 10    | 1.0      | 500               | 288   | 3.21 ± 0.14              | 6.42 ± 0.29                  |
| 11    | 1.0      | 350               | 278   | 1.72 ± 0.03              | 4.91 ± 0.10                  |
| 12    | 1.0      | 350               | 283   | 2.22 ± 0.07              | 6.34 ± 0.20                  |
| 13    | 1.0      | 350               | 288   | 2.51 ± 0.07              | 7.17 ± 0.18                  |
| 14    | 1.0      | 350               | 293   | 3.24 ± 0.14              | 9.25 ± 0.39                  |
| 15    | 1.0      | 350               | 298   | 3.60 ± 0.17              | 10.28 ± 0.43                 |
| 16    | 1.0      | 50                | 288   | 2.21 ± 0.06              | 44 ± 1.2                    |
| 17    | 1.0      | 100               | 288   | 3.96 ± 0.16              | 40 ± 2.2                    |
| 18    | 1.0      | 200               | 288   | 7.40 ± 0.21              | 37 ± 1.2                    |

1 k_{obs'} = k_{obs} - k_{cat}, where k_{cat} = 1.0 × 10^{-4}, 1.05 × 10^{-4}, 1.17 × 10^{-4}, and 1.53 × 10^{-4} s^{-1} at 283, 288, 293, and 298 K, respectively. 2 3HeO₂.

Figure 12. Stoichiometric 3-PhIO–mediated Baeyer–Villiger oxidation of cyclohexanone. (a) Dependence of the reaction rates on the complex concentration [Cyclohexanone] = 0.35 M, T = 15 °C, the iron(III) intermediate (3-PhIO) intermediate was generated with PhIO, in MeCN; (b) Eyring plots. [J] = 10^{-3} M, [cyclohexanone] = 0.35 M in MeCN, at different temperature.

The low activation enthalpies and the large negative activation entropies are typical of associative processes. Almost the same values were observed for the (µ-oxo)(µ-1,2-peroxo)diiron(III)–mediated Baeyer–Villiger reaction (ΔH = 22 ± 1 kJ mol⁻¹ and ΔS = −170 ± 10 J mol⁻¹ K⁻¹) [39].

In view of the kinetic and spectroscopic results obtained for the co-oxidants used, three different kinds of reaction mechanisms can be proposed (Scheme 2). Based on our previously published results with benzaldehydes [36,39], the Baeyer–Villiger reaction is likely to occur through the µ-1,2-peroxo-diiron(III) intermediate by the use of H₂O₂ as cooxidant (Scheme 2A). Since the formation of the peroxo species is fast, the rate-determining step is its reaction with the appropriate carbonyl compounds in a nucleophilic addition reaction.
(A_N). Similar mechanisms can be proposed for 3PhIO, 3mCPBA, and 3BA/0_3 containing systems, where, based on EPR and Raman measurements, nucleophilic Fe^{II}(OIPh) and Fe^{III}(OO(O)CPH) adducts can be deduced as key oxidants (Scheme 2B). It should be noted, however, that based on our previous and current results, we have found no evidence for the formation of characteristic oxoiron(IV) species [34] and their possible role in the oxidation of cyclohexanone via electrophilic OAT mechanism (Scheme 2C).

![Scheme 2. Plausible mechanisms for the peroxo-diiron(III)-mediated Baeyer–Villiger oxidation of cyclohexanone to ε-caprolactone.](image)

### 3. Experimental Section

#### 3.1. Materials and Methods

All syntheses were performed under an argon atmosphere unless stated otherwise. Solvents used for the synthesis and reactions were purified by standard methods and stored under argon. The starting materials for the ligand are commercially available, and they were purchased from Sigma-Aldrich (Budapest, Hungary). The ligands 2-(2′-pyridyl)benzimidazole (PBI), 2-(2′-pyridyl)benzthiazole (PBT), 2-(2′-pyridyl)benzoxazole (PBO), and their complexes [Fe^{II}(PBO)\(_2\)(CF\(_3\)SO\(_3\))] (1), [Fe^{II}(PBT)\(_2\)(CF\(_3\)SO\(_3\))] (2), and [Fe^{II}(PBI)\(_3\)](CF\(_3\)SO\(_3\)) (3), were prepared as previously described [40]. Microanalyses were conducted by the Microanalytical Service of the University of Pannonia. The UV-Visible spectra were recorded on an Agilent 8453 diode-array spectrophotometer using quartz cells. GC analyses were performed on an Agilent 7820A (Budapest, Hungary) gas chromatograph equipped with a flame ionization detector and a 30 m HP-5 column. GC-MS analyses were carried out on Shimadzu QP2010SE (Budapest, Hungary) equipped with a secondary electron multiplier detector with conversion dynode and a 30 m HP-5MS column. Raman and EPR spectra were recorded at \(\lambda_{exc} 785 \text{ nm}\) using a Perkin Elmer Raman Station at room temperature and Bruker ECS106 spectrometer in liquid nitrogen (77 K), respectively.

#### 3.2. Catalytic Oxidations and Determination of Products

All reactions were carried out in a 20 mL Schlenk tube equipped with a condenser. Cyclohexanone (1.00 \(\times\) 10\(^{-2}\) M), complex (1.00 \(\times\) 10\(^{-3}\) M), acetonitrile (5 mL), and the initiator benzaldehyde derivatives or mCPBA (1.50 \(\times\) 10\(^{-1}\) M) were added, and then the mixture was stirred at 60°C under an oxygen atmosphere 5–15 h. Unfortunately, the use of PhIO under catalytic conditions was not technically feasible because of solubility problems. The products were identified by GC (Agilent 7820A) and GC-MS (Shimadzu QP2010SE), and yields and conversions were calculated based on the amount of cyclohexanone con-
sumed and products formed in the reactions using bromobenzene as an internal standard. High selectivity was achieved in all runs, and the calculated yields and conversions were almost identical (<5%).

3.3. Stoichiometric Oxidations

Complex 3 (0.5–2.0 × 10⁻³ M) was dissolved in acetonitrile (1.5 mL), then 4 equivalents of mCPBA or PhIO (or BA under air) were added to the solution. Cyclohexanone (0.1–0.35 M) was added to the solution, and the reaction was monitored with UV–Vis spectrophotometer (Agilent 8453, Budapest, Hungary) at 760 nm (ε = 1360 M⁻¹ cm⁻¹). The Baeyer–Villiger products (lactones) were identified by GC (Agilent 7820A) and GC-MS (Shimadzu QP2010SE).

4. Conclusions

In conclusion, we previously found that N4Py-based iron(II) complexes are capable of carrying out Baeyer–Villiger oxidation of cycloketones via the formation of oxoiron(IV) intermediate [34]. As a continuity of this study, efforts have been made to enhance the catalytic activity by the use of n-heterocyclic ligands and investigate the effect of the ligand framework. Comparing the reactions of [Fe^II(PBO)₂(CF₃SO₃)₂] (1), [Fe^II(PBT)₂(CF₃SO₃)₂] (2), and [Fe^II(PBD)₃](CF₃SO₃)₂ (3) towards cyclohexanone under the same conditions, the relative reactivity is in the order of 1 > 2 > 3 for both mCPBA and in situ-generated PBA (BA with benzaldehyde) systems. In the case of [Fe^II(PBI)](CF₃SO₃)₂ (3), depending on the co-oxidant (H₂O₂, mCPBA, and PhIO) used, we have found strong evidence for the formation of µ-1,2-peroxo-diiron(III), acylperoxo-, and iodosylbenzene-iron(III) intermediates, respectively, and their key role in the Baeyer–Villiger reaction via Aₙ mechanism. To the best of The authors’ knowledge, this is the second example of a peroxo-mediated catalytic Baeyer–Villiger reaction.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27092814/s1, Figure S1: rRaman spectra of 3PhIO, 3H₂O₂ and 3mCPBA complexes; Figure S2: EPR spectra of 3PhIO, 3H₂O₂ and 3mCPBA complexes.

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