Very Important Paper

A Mechanistic Study on the Reaction of Non-Heme Diiron (III)-Peroxido Complexes with Benzoyl Chloride

Markus Lerch,[a] Andreas J. Achazi,[b] Doreen Mollenhauer,[b] Jonathan Becker,[a] and Siegfried Schindler*[a]

Dinuclear iron peroxido complexes are important intermediates for selective oxidation reactions. A detailed kinetic study of the reaction of benzoyl chloride (BzCl) with a dinuclear iron non-heme cis end-on peroxido complex with the ligand EtHPTB (N,N,N,N′-tetraakis(N-ethyl-2-benzimidazolyl)methyl)-2-hydroxy-1,3-diamino-propane) had been performed. The starting complex, the iron peroxido complex, can be obtained either by reaction of the iron(II) complex with O₂ or instead, applying the corresponding iron(III) complex together with hydrogen peroxide. Using low temperature stopped-flow measurements allowed to obtain activation parameters and in combination with a Hammet plot it was possible to postulate a mechanism for the formation of a perbenzoate complex prior to its decomposition. Furthermore, the direct reaction of the dinuclear iron(III) EtHPTB complex with peracetic acid was analyzed. Additionally, in comparison a mononuclear non-heme iron complex with the ligand bztpen (N-benzyl-N,N,N′-tris(2-pyridylmethyl)ethane-1,2-diamine) was investigated as well.

Introduction

Selective oxidation/oxygenation reactions of organic substrates are important in the lab and in industry.[1] Efforts to substitute oxidants that are either expensive and/or quite toxic, e.g. chromium(VI) compounds, led to an intensive research on the development of functional model complexes for the active sites of metalloenzymes, especially oxygenases.[2] For example cyanobacterial aldehyde dehydrogenase catalyzes the conversion of fatty aldehydes into alkanes and formate.[3] Recently Kaizer and co-workers reported the complex [Fe₃⁺(μ-O₂)(MeBzim-Py)₂(MeCN)]₄⁺ as a functional model for this enzyme by applying an iron complex with the ligand MeBzim-Py (2-(2'-pyridyl)-N-methylbenzimidazole; Scheme 1). In that context they furthermore pointed out the mechanistic versatility of peroxido-diiron(III) intermediates.[4]

We and others have been investigating in great detail the reactivity of iron complexes with the ligand RHPTB (Scheme 1) towards dioxygen and hydrogen peroxide.[5] The dinuclear iron (II) complex [Fe₂(EtHPTB)(OBz)]²⁺ (1a, R = Et; EtHPTB = N,N,N′-tetraakis([N-ethyl-2-benzimidazolyl]methyl)-2-hydroxy-1,3-diaminopropane) reacts with O₂ to the cis end-on peroxido complex [Fe₂(EtHPTB)(μ-1,2-O₂)(OBz)(X)]⁺ (2a, X = solvent or co-ligand).[5b] While under these conditions the formed peroxido complex is only persistent for a short time, it is possible to increase its stability by preparing it from the corresponding iron (III) complexes, [Fe₂(RHPTB)(X)]ⁿ⁺ in combination with hydrogen peroxide.[5b] This reaction was investigated in acetonitrile as well as in methanol leading to the same results.[6] Furthermore, the reaction of the mononuclear iron(III) complex [Fe₂(bztpen)(OMe)](ClO₃)₂ (3(ClO₃)₂; bztpen = N-benzyl-N,N,N′-tris(2-pyridylmethyl)ethane-1,2-diamine) with hydrogen peroxide had been analyzed.[7] An end-on hydroperoxido complex was formed that could be transformed into a side-on peroxido species after the addition of a base.[7b] Interestingly, the corresponding iron (II) complex did not react with dioxygen (neither with carbon monoxide), only with nitrogen oxide a reaction occurred.[7d]

With regard to the formation of percarboxylate species as important intermediates in oxygenation reactions we report herein our results on the reaction of the iron(III) peroxido complex with EtHPTB as ligand and benzoyl chloride (BzCl) together with some related reactions.

Results and Discussion

The iron(III) complex [Fe₂(EtHPTB)(OH)₂(MeOH)₂](ClO₃)₃ (1b-(ClO₃)₃) was prepared in good yields by reacting the ligand
EtHPTB with iron(III) perchlorate and Et₃N in methanol. The molecular structure of 1b is shown in Figure 1 (crystallographic data of 1b(ClO₄)₃ are reported in the Supporting Information; Figure S2). The molecular structure of this complex is very similar to the complex [Fe₂(EtHPTB)(H₂O)(OMe)(MeOH)][ClO₄]₄ that had been reported previously by Avenier et al.⁸ Here, water molecules are coordinated instead of hydroxide anions and one of the methanol ligands is deprotonated. A direct comparison of the two structures reveals that the angle spanned between the iron centers and the alcoholate oxygen is somewhat larger (angle Fe₁-O₁-Fe₂: Avenier 131.1°; this work 128.5°) and this also results in a greater distance between the iron centers (distance Fe₁-Fe₂: Avenier 3.65 Å; this work 3.61 Å). In contrast to our synthetic protocol described herein, the authors did not apply triethylamine to prepare the iron(III) complex and did not recrystallize the product. Furthermore, 1b can be compared with [Fe₂(HPTB)(μ-OH)(NO₃)]₂(NO₃)₂ that had been investigated previously.⁹

Reaction of 1b with H₂O₂

When a solution of 1b(ClO₄)₃ was reacted with hydrogen peroxide in methanol, a color change from a pale yellow color to a turquoise color was observed, which indicates the formation of an iron peroxido complex (2b, Scheme 2) as described previously (Figure 2).⁵b ESI-MS measurements support the assumption that the formation of the peroxido complex [{Fe₂(EtHPTB)(μ-1,2-O₂)(OH)(H₂O)}+ + MeOH]²⁺ is the main species under these conditions (compare Figure S5 and S6). One equivalent of H₂O₂ is enough for complete formation of 2b (Figure S9). The reaction in methanol is quite fast (completed within 1 s at RT) and the turquoise-colored solution is stable for a few minutes under these conditions. As previously described, this reaction can be followed by applying stopped-flow techniques.⁵b Time-resolved spectra are shown in Figure 3.

The peroxido complex is characterized by the main absorbance at 605 nm with a molar attenuation coefficient ε of 2200 L mol⁻¹ cm⁻¹ under our conditions which compares well with data of the literature with other solvents.⁵b,c Absorbance vs. time traces under pseudo-first-order conditions ([H₂O₂] ≫ [1b]) could be fitted using single exponential functions. As observed previously a plot of the obtained rate constants kobs vs. the hydrogen peroxide concentration at different temperatures exhibited a linear dependence without

Figure 1. Complex 1b [Fe₂(EtHPTB)(OH)₂(MeOH)₂][ClO₄]₃⁺ (left). Molecular structure (ORTEP drawing: 50% probability) of the cation of 1b(ClO₄)₃·3 MeOH. Uncoordinated 3 perchlorate anions and 3 methanol molecules are omitted for clarity (right).

Figure 2. Reaction of 1b with hydrogen peroxide, followed by the addition of benzoyl chloride.

Figure 3. Time-resolved UV-vis spectra (Δt = 0.03 s) of the reaction between complex 1b (c = 0.4 mmol L⁻¹) and hydrogen peroxide (c = 20.0 mmol L⁻¹) at 25.0°C in methanol (concentrations after mixing). The inset shows the time-trace of the reaction.
an intercept (Figure 4) and thus leading to an overall second-order rate law (Equation 1).

\[
\frac{d[2b]}{dt} = k_2 [1b] [H_2O_2]
\] (1)

An Eyring plot of the derived second-order rate constants over a much larger temperature range from –50.0 to +25.0 °C (Figure 5) allowed the calculation of the activation parameters to \( \Delta H^\circ = 46 \pm 1 \text{ kJ mol}^{-1} \) and \( \Delta S^\circ = -40 \pm 2 \text{ J mol}^{-1} \text{K}^{-1} \). Data compare reasonable well with previous results of the [Fe₂(HPTB)(μ-ΟΗ)(NO₃)]₂(NO₃)₂ with \( \Delta H^\circ = 53 \pm 3 \text{ kJ mol}^{-1} \) and \( \Delta S^\circ = -17 \pm 1 \text{ J mol}^{-1} \text{K}^{-1} \) (see Table 1).[b]

**Reaction of 2b with benzoyl chloride**

The reaction of the peroxydo complex 2b with BzCl was investigated in methanol because no reaction was observed in acetonitrile (only decomposition of 2b was detected). Furthermore, we did not assert an influence of different R-groups in R-HPTB (Scheme 1) on the reactivity. Iron(III) complexes with the unsubstituted ligand HPTB (R=H) and BnHPTB (R=Bn) showed the same reactivity towards H₂O₂ and the subsequent reaction with benzoyl chloride. As shown in Figure 2 a rapid color change to a gold-brown-colored solution was observed when 2b was reacted with benzoyl chloride in excess. Time-resolved UV-vis-spectra were recorded in stopped-flow measurements at low temperatures (Figure 6).

The decay of the absorbance maximum at 605 nm of 2b (premixed immediately prior to the measurement applying an excess of H₂O₂) can be observed while at the same time a new compound is formed, characterized with an absorbance maximum at 445 nm. Two isosbestic points are observed at 415 and 515 nm. Absorbance vs. time traces again could be fitted perfectly well to a single exponential function, however a plot of \( k_{obs} \) vs. \( c(\text{BzCl}) \) turned out to be nonlinear. Instead, to obtain a linear correlation, it was necessary to plot \( k_{obs} \) vs. \( c(\text{BzCl})^2 \) (Equation 2).

\[
\frac{d[12]}{dt} = k_3 [2b] [\text{BzCl}]^2
\] (2)

Third-order rate constants obtained here (\( k_{365} = 9.7 \pm 0.3 \times 10^5 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1} \)) compare well with those measured for other

---

**Table 1.** Summary of molar attenuation coefficient, rate constants and activation parameters of the kinetically investigated reactions in this study.

| Reaction in MeOH | BzCl derivative | \( \lambda_{max} \) [nm] | \( k_{2 \text{ MeOH}} \) [L mol⁻¹ s⁻¹] | \( \Delta H^\circ \) [kJ mol⁻¹] | \( \Delta S^\circ \) [J K⁻¹ mol⁻¹] |
|------------------|------------------|---------------------------|-------------------------------|-----------------------------|-----------------------------|
| 1b + H₂O₂ (→ 2b) | BzCl             | 600                       | 568±2                         | 46±1                        | -40±2                       |
| 2b + BzCl (→ 12) | BzCl             | 600                       | 9.7 (±0.3) 10⁻¹ [a]           | 40±1                        | 11±3                        |
|                  | BzCl             | 600                       | 9.7 (±0.3) 10⁻¹ [a]           | 40±1                        | 11±3                        |
|                  | BzCl             | 600                       | 9.7 (±0.3) 10⁻¹ [a]           | 40±1                        | 11±3                        |
|                  | BzCl             | 600                       | 9.7 (±0.3) 10⁻¹ [a]           | 40±1                        | 11±3                        |
|                  | BzCl             | 600                       | 9.7 (±0.3) 10⁻¹ [a]           | 40±1                        | 11±3                        |
|                  | BzCl             | 600                       | 9.7 (±0.3) 10⁻¹ [a]           | 40±1                        | 11±3                        |
|                  | BzCl             | 600                       | 9.7 (±0.3) 10⁻¹ [a]           | 40±1                        | 11±3                        |
| 2a + BzCl (→ 12) | BzCl             | 450                       | 243±10 [b]                    | -36±1                       | -33±6                       |
| 1b + PAA         | 440              | 455 ±125 [c]              | 32±1                         | -48±6                       |

[a] \( k_2 \) third-order constant. ND = not determined. [b] At \( -60 \text{ °C} \). [c] At \( -65 \text{ °C} \).

---

**Figure 5.** Eyring plot for the reaction of complex 1b (\( c = 0.4 \text{ mmol L}^{-1} \)) with H₂O₂ (\( c = 20 \text{ mmol L}^{-1} \)) in the temperature range from \(-50.0 \) to \(+25.0 \text{ °C} \).

**Figure 6.** Time-resolved UV-vis spectra (\( \Delta t = 7.4 \text{ s} \)) of the reaction between 2b (\( c = 0.2 \text{ mmol L}^{-1} \), obtained by premixing 1b with an excess of H₂O₂) and BzCl (\( c = 20.0 \text{ mmol L}^{-1} \)) at \(-80.0 \text{ °C} \). Molar attenuation coefficient \( \varepsilon_{445} = 4300 \text{ L mol}^{-1} \text{ cm}^{-1} \). The inset shows the time-traces of the reaction.
reactions that showed a third-order rate law e.g. NO + O₂ with a rate constant of 2.1 × 10⁶ L s⁻¹ mol⁻² at 25 °C [10] (depending on the conditions slightly different values) [11] in aqueous solutions and non-aqueous media were obtained. [12]

Since the sole kinetic interpretation does not yet provide any evidence that exactly two benzoyl chloride molecules react with the peroxido complex, a substoichiometric addition was also carried out here. A clear linearity can be seen up to the second equivalent benzoyl chloride added (Figure S10). This observation supports the assumption that exactly two molecules of benzoyl chloride react with 2b during the reaction with benzoyl chloride. Furthermore, to exclude that benzoyl peroxide is an active reagent herein (it is synthesized in industry from benzoyl chloride with hydrogen peroxide in alkaline solutions), several test reactions with ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt) were performed. ABTS is a reagent that is used to detect radicals and non-aqueous media were obtained. [12]

Hammett Plot

The Hammett correlation (a linear free energy relationship) is a widely used method to evaluate the impact of electrosterical effects on reactions. This correlation allows conclusions to be drawn about the transition state of the rate-determining step (RDS) of the observed reaction. Figure 8 shows the Hammett plot for the reaction of 2b with para-substituted benzoyl chloride. In this study only para-substituted benzoyl chlorides were used, due to possible steric hindrance of meta-substituents. The Hammett plot leads to a V-shape from the two linearly fitted points that intersect near by a σ-value of 0 (unsubstituted BzCl).

Overall it is obvious, that electron-withdrawing (pCl, pNO₂) and electron-donating (pN(Me)₂, pOMe, pMe) substituents slowed down the reaction. The V-shape indicates a change in the reaction mechanism, in which the electron-rich pN(Me)₂-BzCl is more nucleophilic (ρ = −1.996) and the electron-poor pNO₂-BzCl is more electrophilic (ρ = 0.477). This provides

\[
[\text{Fe}_{2}(\text{EtHPTB})(\text{OOBz})(\text{OH})_2]^{2+} \quad \text{with} \quad m/z = 502.1 \quad \text{as a direct derivative of 11 (Figure S7). The formation of methyl benzoate and benzoic acid anhydride could be a hint of a free radical mechanism (iron(IV)oxido/benzoato radical-pathway), as these products are formed due to recombination reactions.}

For a more detailed analysis we applied para-substituted BzCl derivatives with the electron-withdrawing groups −Cl, −NO₂ and electron-donating groups −N(Me)₂, −OMe, −Me for the reaction with 2b. Besides BzCl (temperature range between −80.0 and 0.0 °C) we performed measurements with pN(Me)₂-BzCl and pNO₂-BzCl in a temperature range between 15.0 and 50.0 °C. From the temperature dependence the corresponding Eyring plots (Figure S11) allowed calculations of the activation parameters with BzCl: ΔH° = 40 ± 1 kJ mol⁻¹ and ΔS° = 10 ± 3 J mol⁻¹ K⁻¹; pN(Me)₂-BzCl: ΔH° = 69 ± 1 kJ mol⁻¹, ΔS° = 39 ± 2 J mol⁻¹ K⁻¹; pNO₂-BzCl: ΔH° = 67 ± 3 kJ mol⁻¹, ΔS° = 21 ± 8 J mol⁻¹ K⁻¹ (see Table 1). The slightly positive activation entropies indicate a dissociative interchange mechanism.

Figure 7. Plot of \(k_{\text{obs}}\) vs. \(c(\text{BzCl})^2\) at different temperatures. Concentration \(c(2b) = 0.2\ \text{mmol}\ L^{-1}\).
valuable information about the location of the RDS and transition state (TS). The strong negative \( \rho \)-value clearly indicates a build-up of a positive charge in the TS of the RDS, whereas the slightly positive \( \rho \)-value indicates a build-up of a positive charge in the TS of the RDS. In combination with the slightly positive activation entropies of the reaction between 2b and \( \rho \text{NO}_2\)-BzCl resp. \( \rho \text{N(Me)}_2\)-BzCl (indicating a dissociative interchange mechanism) two different reaction pathways can be proposed. A possible mechanism for both reaction pathways is presented in Scheme 3.

In the reaction pathway with \( \rho \text{N(Me)}_2\)-BzCl, the C–Cl bond is severely weakened or even broken in the TS of the RDS, which is due to the high positive charge on the carbonyl carbon. On the other hand, the slightly positive \( \rho \)-value in the \( \rho \text{NO}_2\)-BzCl reaction pathway can be interpreted as a partially accomplished nucleophilic attack on the carbonyl carbon of the benzoyl chloride. In any case, it can be confirmed that benzoyl chloride is actively involved in the RDS of the whole reaction sequence.

In contrast to our system, no effect on para-substitution was observed with the system of Kripli and co-workers, where a \( \rho \)-value of zero was obtained.\(^6\) Therefore, for their reaction mechanism a nucleophilic attack of the peroxydiiron(III) complex as rate-determining step had been excluded.

**Reaction of iron(II) complex 1a with O\(_2\) and benzyol chloride**

As described in the introduction, the iron(II) complex \( [\text{Fe}_2(\text{EthPTB})(\text{OBz})]^{2+} \) (crystallographic data of 1a(BPh)_2 are reported in the Supporting Information; see Figure S1) reacts with dioxygen to form the peroxy complex 2a (Scheme 2).

To gain further support for the proposed mechanism of the reaction of 2b with BzCl we also investigated the reaction of 2a with BzCl (the benchtop experiment is reported in the Supporting Information, Figure S12 and S13). To accomplish this we used a double-mixing stopped-flow unit with four syringes (syringe 1: solution of 1a; syringe 2: solvent saturated with dioxygen; syringe 3: solvent saturated with argon; syringe 4: solution of BzCl). Because of the poor solubility of 1a(BPh)_2 in MeOH, the reaction was performed with 5% MeCN as co-solvent. Time-resolved UV-vis spectra of this reaction are presented in Figure 9.

A plot of the \( k_{\text{obs}} \)-values vs. BzCl-concentration allowed a linear fit with an intercept C (Figure S13) leading to an overall second-order rate law (Equation 3).

\[
\frac{d[12]}{dt} = k_2 [2a] [\text{BzCl}] + C
\]

The reaction is a bit faster than the reaction of 2b with BzCl. However, this is easy to understand because here a benzoate is already coordinated to the complex and therefore only has to react further with BzCl. Overall, this supports our postulated mechanism (Scheme 2). The reaction was measured in a temperature range between –70.0 and –40.0 °C and from an Eyring plot (Figure S14) of the second-order rate constants the activation parameters could be calculated to \( \Delta H^\circ = 36 \pm 1 \text{ kJ mol}^{-1} \) and \( \Delta S^\circ = -33 \pm 6 \text{ J mol}^{-1} \text{K}^{-1} \) (see Table I). The slightly negative activation entropy indicates an interchange associative mechanism, again in accordance with our postulated mechanism. The intercept we observed for the plot of the \( k_{\text{obs}} \)-values vs. c(BzCl) (Figure S14) is a bit more difficult to interpret. While we think we can exclude a reversible reaction at this point it could be possible that to some part acetonitrile is coordinated that needs to dissociate prior to the bonding of BzCl, leading to a reaction step independent of (BzCl) and thus causing an intercept. However, it also could be caused by the equilibrium between 2a and I1.

---

**Scheme 3.** Postulated mechanisms in dependence on different benzyol chloride derivatives (electron-withdrawing or electron-donating groups in para position).
To gain further insights into the reaction from 2b with benzoyl chloride via the (assumed) I1, 2a and (assumed) I2 to give a possible product P, a computational analysis was performed. The equilibrium structures and Gibbs energies of the involved complexes in solution were calculated with DFT for the concentrations used in the experiment (see Computational details). The results of the calculations are shown in Scheme 4.

The low-spin state with 0 unpaired electrons (singlet state with total spin quantum number $S = 0$), the triplet state ($S = 3$), nonet state ($S = 4$) and the high-spin state with 12 unpaired electrons (tridecet quintet state ($S = 6$)) have been calculated for this step, but all are energetically unfavorable for 2b, I1-a, 2a and I2-a. Instead, the undecet spin state ($S = 5$) is most favorable for these iron complexes. The other iron complexes (Scheme 4) are very similar to 2b, I1-a, 2a and I2-a; therefore, we calculated them in an undecet spin state ($S = 5$) as well. For the first step we assume that 2b reacts to I1-a (see Scheme 4). The reactions is exergonic and a Gibbs energy of $-48.1 \text{kJ mol}^{-1}$ is gained. Three additional isomers (I1-b to I1-d) have been calculated for this step, but all are energetically less favorable. I1-a and I1-c are in agreement with the structures proposed in Scheme 2. The benzoate radical in complexes I1-c and I1-d is only loosely attached to the rest of the complex via π-π interaction and C-H-O hydrogen bonds. Thus, the iron atoms remain Fe$.^{\text{II}}$. Furthermore, the spin state of the benzoate radical should have nearly no effect on the rest of the complex due to the large distance or loose attachment. Indeed, the nonet spin state ($S = 4$) for I1-c and I1-d is energetically only $+0.1 \text{kJ mol}^{-1}$ higher than the undecet spin state ($S = 5$) for the same molecular structure.

Next an intramolecular formation takes place in I1-a, water is released, methanol binds to one iron atom resulting in 2a. The reaction is exergonic and a Gibbs energy of $-78.0 \text{kJ mol}^{-1}$ is gained. From there, we assume that 2a reacts to I2-a and a Gibbs energy of $-33.8 \text{kJ mol}^{-1}$ is gained. The shortest bond distance between an oxygen atom of the benzoate radical and the Fe$^{2+}$-O group of the undecet I2-a is 2.99 Å. This is a very long, and therefore, a weak bond. For comparison the bond distance between the benzoate anion and the Fe-Cl group of the undecet I2-a is only 1.96 Å. Like for I1-c and I1-d, the spin state of the loosely attached benzoate radical has nearly no effect on the rest of the I2-a complex. Hence, the nonet spin state is energetically very close to the undecet spin state (only $+0.5 \text{kJ mol}^{-1}$ higher for the same molecular structure). As shown in Scheme 4, the benzoate radical in I2-a can react to a peroxbenzoate (I2-b). This intramolecular reaction is exergonic by $-21.5 \text{kJ mol}^{-1}$ and both, the third oxygen of the peroxbenzoate and the chloride form weak bonds to the iron, which is connected to the peroxbenzoate. These results are in agreement with the proposed reaction in Scheme 2.

A possible next step is the intramolecular formation of a hypohor chloride (P-a). The hypohor chloride can reorient itself forming P-b, which is the most stable complex found in this study. The reaction from 2a over I2-a, I2-b, and P-a up to P-b is thermodynamically favorable. The formations of I2-a, I2-b, and P-a involve either the breaking or formation of an oxygen-oxygen bond as a key step. Thus, possible reaction barriers can be expected to be similar in all these cases.

Reactions of 1b with peracids

To gain a better understanding of the overall mechanistic scenario 1b was furthermore reacted with percarboxylic acids. We excluded perbenzoic acid due to the danger involved with this compound and chose peracetic acid (PAA), m-chloroperbenzoic acid (mCPBA) and perdecanoic acid (PDA) instead. Perdecanoic acid was prepared according to the synthesis reported by Sitko et al., however, so far no crystal structure of this compound had been reported.$^{[15]}$ We obtained crystals of perdecanoic acid and the molecular structure together with crystallographic data are presented in the Supporting Information (Figure S4 and Table S4).

When 1b was reacted with an excess PAA in methanol, an orange-brown-colored solution formed (Figure S15) and peracetic acid adduct compounds could be detected in an ESI-MS spectrum (Figure S8). A $m/z$ ratio at 1123.1 shows the presence of the peracetato complex $[^{15}\text{Fe},(\text{EtHPTB})(\text{OOAc})(\text{OH})](+2\text{ClO}_2)^-$. In Figure 10 the characteristic UV-vis bands of the intermediates (1a + O$_2$ + BzCl, 1b + H$_2$O$_2$ + BzCl and 1b + PAA) are compared.

Comparison with data from the literature for UV-vis data for iron(III) peroxyacetate complexes (in acetoniitrile) are in accordance with our data and therefore also support our assignment of a peroxybenzoate complex discussed above.$^{[16]}$

Efforts to crystallize and structurally characterize the intermediates I1/I2 have been unsuccessful. So far (to the best of our knowledge) only one example of a structurally character-
Reactions with NEt$_3$

If the percarboxylate complex formed by the reaction of 2b + BzCl was reacted with NEt$_3$, a peroxido complex formed (the benchtop reaction is shown in Figure S18). Time-resolved spectra of the reaction of NEt$_3$ with premixed 2b + BzCl were obtained again with our double-mixing stopped-flow unit with four syringes and are presented in Figure 11. A plot of $k_{obs}$ vs. [NEt$_3$] showed a linear dependence with intercepts (Figure S19). This indicates a parallel or back reaction, most likely based on an acid/base equilibrium under the conditions applied.

An Eyring plot obtained from the $k_2$ values of the main reaction (Figure S20) did lead to the activation parameter $\Delta H^\ddagger = 49 \pm 1$ kJ mol$^{-1}$, $\Delta S^\ddagger = 9 \pm 4$ J mol$^{-1}$ K$^{-1}$. With an activation entropy close to 0 this reaction follows an interchange pathway. The same reaction behavior was observed when premixed 1a + PAA (instead of 2b + BzCl) was reacted with NEt$_3$.

Reaction of [Fe(bztpen)OOH]$^{2+}$ with BzCl

To compare our results of a dinuclear iron complex system with a mononuclear iron complex we also investigated the reaction of the iron(III) complex with bztpen as ligand (Scheme 1). The complex [Fe(bztpen)(OMe)](ClO$_4$)$_2$ (3) has been prepared under aerobic conditions in methanol by combining bztpen, Fe(ClO$_4$)$_2$ and Et$_3$N in a ratio of 1:1:1. Crystals were obtained and the molecular structure together with crystallographic data are reported in the Supporting Information (Figure S3 and Table S3). The molecular structure compares well with [Fe$^{11-}$(bztpen)(OMe)][PF$_6$]$_2$ reported previously.$^{[18]}$ It is well known from previous work that this complex reacts with hydrogen peroxide to a purple-colored $end$-on hydroperoxido complex, [Fe(bztpen)(OOH)]$^{2-}$. Time-resolved UV-vis spectra of this reaction are reported in the Supporting Information (Figure S21).

Reactions with PDA

The diagram in the right corner shows the time-trace over the course of 20 s. If the percarboxylate complex formed by the reaction of 2b + BzCl was reacted with PDA, a peroxido complex formed (the benchtop reaction is shown in Figure S18). Time-resolved spectra of the reaction of PDA with premixed 2b + BzCl were obtained again with our double-mixing stopped-flow unit with four syringes and are presented in Figure 11. A plot of $k_{obs}$ vs. [PDA] showed a linear dependence with intercepts (Figure S19). This indicates a parallel or back reaction, most likely based on an acid/base equilibrium under the conditions applied.

An Eyring plot obtained from the $k_2$ values of the main reaction (Figure S20) did lead to the activation parameter $\Delta H^\ddagger = 49 \pm 1$ kJ mol$^{-1}$, $\Delta S^\ddagger = 9 \pm 4$ J mol$^{-1}$ K$^{-1}$. With an activation entropy close to 0 this reaction follows an interchange pathway. The same reaction behavior was observed when premixed 1a + PAA (instead of 2b + BzCl) was reacted with PDA.

Reaction of [Fe(bztpen)OOH]$^{2+}$ with BzCl

To compare our results of a dinuclear iron complex system with a mononuclear iron complex we also investigated the reaction of the iron(III) complex with bztpen as ligand (Scheme 1). The complex [Fe(bztpen)(OMe)](ClO$_4$)$_2$ (3) has been prepared under aerobic conditions in methanol by combining bztpen, Fe(ClO$_4$)$_2$ and Et$_3$N in a ratio of 1:1:1. Crystals were obtained and the molecular structure together with crystallographic data are reported in the Supporting Information (Figure S3 and Table S3). The molecular structure compares well with [Fe$^{11-}$(bztpen)(OMe)][PF$_6$]$_2$ reported previously.$^{[18]}$ It is well known from previous work that this complex reacts with hydrogen peroxide to a purple-colored $end$-on hydroperoxido complex, [Fe(bztpen)(OOH)]$^{2-}$. Time-resolved UV-vis spectra of this reaction are reported in the Supporting Information (Figure S21).

Reactions with NEt$_3$

If the percarboxylate complex formed by the reaction of 2b + BzCl was reacted with NEt$_3$, a peroxido complex formed (the benchtop reaction is shown in Figure S18). Time-resolved spectra of the reaction of NEt$_3$ with premixed 2b + BzCl were obtained again with our double-mixing stopped-flow unit with four syringes and are presented in Figure 11. A plot of $k_{obs}$ vs. [NEt$_3$] showed a linear dependence with intercepts (Figure S19). This indicates a parallel or back reaction, most likely based on an acid/base equilibrium under the conditions applied.

An Eyring plot obtained from the $k_2$ values of the main reaction (Figure S20) did lead to the activation parameter $\Delta H^\ddagger = 49 \pm 1$ kJ mol$^{-1}$, $\Delta S^\ddagger = 9 \pm 4$ J mol$^{-1}$ K$^{-1}$. With an activation entropy close to 0 this reaction follows an interchange pathway. The same reaction behavior was observed when premixed 1a + PAA (instead of 2b + BzCl) was reacted with NEt$_3$.
and kinetic data fit well with our previous results. However, in contrast to the reaction of 2b with BzCl the reaction of [Fe(bztpen)(OOH)]{2−} with BzCl is complex (time resolved UV-vis spectra of this reaction are reported in the Supporting Information, Figure S22), indicating additional reactions take place that so far could not be analyzed.

In a subsequent reaction with a base such as Et3N the hydroperoxido complex reacts to the corresponding side-on peroxido complex (turquoise). Interestingly, while the hydroperoxido complex reacts quite fast with benzoyl chloride the side-on peroxido complex did not react at all with BzCl.

**Summary and Conclusion**

In summary, we have studied the kinetics of the formation of peroxido complex 2b (FeIV complex 1b + H2O2) and the subsequent reaction with benzoyl chloride in methanol in detail. We assume that the chromophore formed with \( \lambda_{\text{max}} = 445 \text{ nm} \) is an iron(IV)oxido-carboxylato radical species \( \text{I1} \) that alternatively had been described as an iron(IV)oxido-carboxylato species (for PAA systems) according to the following equilibria presented in Scheme 5.16-19

It turned out that the peroxido complex 2a, formed in the reaction between FeIII complex 1a and \( \text{O}_2 \), was also able to react in the same way to form the chromophore at \( \lambda_{\text{max}} = 445 \text{ nm} \).

In contrast to previous publications that reported formation of iron(III)percarboxylates (mainly peracetae) in acetonitrile, our intermediates 11/12 herein were formed in the protic solvent methanol. Detailed kinetic studies were performed for the reaction of the peroxido complexes with benzoyl chloride and furthermore, the reaction of the iron(III) complex 1b with peracetic acid.

From our kinetic investigations including a Hammet analysis we could propose a mechanism for the formation of the reactive intermediates, which is supported by a thermodynamic consideration of various intermediates using DFT calculations. They showed that the iron(III) species are more stable than the species with higher oxidized iron. The intermediates finally decompose to an almost colorless mixture of products that only in part could be identified.

**Experimental Section**

**General:** All solvents were distilled before use. Extra dry and oxygen-free solvents were distilled using desiccants under an argon atmosphere. Commercially available chemicals were used without further purification. Abbreviations of the supplier: Alfa Aesar (AA), CARL ROTH (CR), J&K Scientific (J&K), PanReac AppliChem ITW Reagents (PRAC), ACROS ORGANIC (AO), Sigma Aldrich (SA), FluoroChem (FC). Methanol extra dry (AO; 99.9 %), acetonitrile extra dry (AO; 99.9 %), 4-(dimethylamino)benzoyl chloride (J&K, 97 %), 4-methoxybenzoyl chloride (J&K, 99 %), 4-methylbenzoyl chloride (J&K, 99 %), benzoyl chloride (SA; 99 %), 4-chlorobenzoyl chloride (J&K, 99 %), 4-nitrobenzoyl chloride (SA; 99 %), 1,3-diamino-2-propanol-N,N,N',N'-tetraacetic acid (TCI; 98 %), 1,2-phenylenediamine (AA; 98 %), 2-chloromethyl-pyridine hydrochloride (FC; 97 %), \( \text{N} \)-benzylethylenediamine (AA; 98 %), trifluoromethanesulfonic acid (acerb; 99 %), iron powder (AA; 99 %), iron(III) perchlorate nonahydrate (SA; 98 %), iron(III)trifluoracetate (AA; 90 %), benzoic acid (AA; 99 %); decanoic acid (TCI; 98.0%), hydrogen peroxide (CR; 50 % solution in \( \text{H}_2\text{O} \)), peracetic acid (PRAC; 15 % solution in \( \text{H}_2\text{O} \)), urea hydrogen peroxide (SA; 97 %), 2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (AA; 98 %). Pure iron(II) trifluoroacetatoni tritellurium salt was synthesized according to the literature.20

**Physical Measurements:** \( ^1\text{H} \) and \( ^{13}\text{C} \)-NMR spectra were recorded on a Bruker Avance II 200 spectrometer (\( ^1\text{H} \) at 200 MHz; \( ^{13}\text{C} \) at 50 MHz), Bruker Avance II 400 spectrometer (\( ^1\text{H} \) at 400 MHz; \( ^{13}\text{C} \) at 100 MHz) and Bruker Avance III HD 400 spectrometer (\( ^1\text{H} \) at 400 MHz; \( ^{13}\text{C} \) at 100 MHz) in deuterated solvents using TMS as internal standard. The \( ^1\text{H} \)- and \( ^{13}\text{C} \)-NMR spectra were calibrated against the proton and carbon signals of tetramethylsilane.

**ESI-MS Measurements:** Electrospray-ionization MS (ESI-MS) measurements in MeOH were performed on a Bruker micro-TOF mass spectrometer. When measuring any percarboxylato species, the corresponding solutions were pre-cooled to a temperature just above the melting point of methanol using liquid nitrogen. After mixing of the complex and the reagent, the cooled solution was measured immediately.

**Stopped-Flow Technique:** Kinetic studies of the reactions of hydrogen peroxide with iron(III)complexes were recorded on a modified Hi Tech SF-3L low-temperature stopped-flow unit (modification for possible double-mixing measurements; Salisbury, U.K.) equipped with a J&M TIDAS 16-500 diode array spectrophotometer (J&M, Aalen, Germany). The kinetic data were treated by a global analysis fitting routine using the program Kinetic Studio (v.4.0.113798, T &K Scientific) and/or by extracting single absorbance vs. time traces at different wavelengths. These traces were fitted to single-exponential functions using the integrated J&M software Kinspec. Hydrogen peroxide solutions were prepared by adding hydrogen peroxide (50 %, cerimetric titration) with microcippots to the solution. In order to investigate the intermediates 11/12 using the stopped-flow technique, complex 1b was treated with an excess of \( \text{H}_2\text{O}_2 \). This premixed solution is taken up in the stopped-flow syringes and used as usually. For measurements where moisture and or air/oxygen should be avoided, the stopped-flow syringes were prepared in a glovebox by MBraun under an argon atmosphere. The reaction between 1a and \( \text{O}_2 \) and the subsequent reaction with benzoyl chloride was performed with the double-mixing stopped-flow option. Dioxygen concentration in a saturated methanol solution has been reported to be 10.4 mmol L\(^{-1}\) at 25 °C.21

**Computational Details:** All structure optimizations were performed with B3LYP*-D3(BJ)/def2-TZVP,24 the multipole accelerated resolution-of-identity (RI) approximation for \( J \) (MARI-J, with default parameters), Fermi-smearing, the “multiple grid” m4 for the
The def2-SVP basis set was used for all atoms except iron. For iron the def2-TZVP[20] was employed. For MARI-J the default parameter from older Turbomole versions were used to speed up calculations: precision: 10⁻⁶, imaxxom: 10, thrsm: 10⁻¹⁸. The frequency calculations also verified the found molecular structures as minima (at the PBE0-D3(BJ)/def2-SVP, def2-TZVP level of theory).

At the B3LYP*-D3(BJ)/def2-TZVP level of theory various spin states as minima (at the PBE0-D3(BJ)/def2-SVP, def2-TZVP level of theory). Furthermore, Kepp[27] showed that the results for B3LYP* (with 15% HF exchange) can be improved by adding the D3(BJ) dispersion correction of the original B3LYP density functional. The ro-vibrational contributions are calculated for all molecules at the PBE0-D3(BJ)/def2-SVP, def2-TZVP[20,21] level semiempirical with the NumForce script including the fast calculations: precision: 10⁻⁶, parameter from older Turbomole versions were used to speed up calculations: precision: 10⁻⁶, imaxxom: 10, thrsm: 10⁻¹⁸. The concentration is included via the translational entropy. This contribution is included via the translational entropy. This contribution is included via the translational entropy.

The def2-TZVP[20] basis set was used for all atoms except iron. For iron the def2-TZVP[20] was employed. For MARI-J the default parameter from older Turbomole versions were used to speed up calculations: precision: 10⁻⁶, imaxxom: 10, thrsm: 10⁻¹⁸. The frequency calculations also verified the found molecular structures as minima (at the PBE0-D3(BJ)/def2-SVP, def2-TZVP level of theory).

At the B3LYP*-D3(BJ)/def2-TZVP level of theory various spin states as minima (at the PBE0-D3(BJ)/def2-SVP, def2-TZVP level of theory). Furthermore, Kepp[27] showed that the results for B3LYP* (with 15% HF exchange) can be improved by adding the D3(BJ) dispersion correction of the original B3LYP density functional. The ro-vibrational contributions are calculated for all molecules at the PBE0-D3(BJ)/def2-SVP, def2-TZVP[20,21] level semiempirical with the NumForce script including the fast calculations: precision: 10⁻⁶, parameter from older Turbomole versions were used to speed up calculations: precision: 10⁻⁶, imaxxom: 10, thrsm: 10⁻¹⁸. The concentration is included via the translational entropy. This contribution is included via the translational entropy.
NaOH (32 mmol) in 5 mL water was prepared. A third of this solution was stirred for an additional 3 days at room temperature. The product was extracted 3 times with 10 mL dichloromethane. The combined organic phase was extracted with brine. The dichloromethane extract was dried over Na$_2$SO$_4$. The solvent was evaporated and the crude product was purified by column chromatography with silica as stationary phase (elucent: dichloromethane/MeOH). The product was obtained as a pale yellow solid (1.36 g, 3.21 mmol, yield 64%). $^1$H-NMR (400 MHz, CDCl$_3$, TMS): δ = 8.52–8.44 (m, 3H, 3 × Ar–CH$_3$), 7.60–7.53 (m, 3H, 3 × Ar–CH), 7.49–7.39 (m, 3H, 3 × Ar–CH$_2$), 7.32–7.17 (m, 5H, 5 × Ar–CH), 7.14–7.08 (m, 3H, 3 × Ar–CH$_2$), 3.78 (s, 4H, 2 × CH$_2$), 3.72 (s, 2H, –CH$_2$), 3.59 (s, 2H, –CH$_2$), 2.82–2.62 (m, 4H, 2 × CH$_2$). $^{13}$C-NMR (400 MHz, CDCl$_3$, TMS): δ = 150.0 (s, Ar–CH$_2$), 148.9 (s, Ar–C$_3$), 136.3 (s, Ar–CH$_2$), 128.8 (s, Ar–C$_2$), 128.2 (s, Ar–CH$_2$), 126.9 (s, Ar–C$_2$), 122.8 (s, Ar–C), 121.6 (s, Ar–CH$_2$), 121.6 (s, Ar–CH$_2$), 60.8 (s, 2 × CH$_2$), 60.6 (s, –CH$_2$), 59.0 (s, –CH$_3$), 52.2 (s, –CH$_3$), 51.4 (s, –CH$_3$). MS (ESI): $m/z = [M+H]^+ = 424.25$.

**Synthesis of [Fe(bztpen)(OMe)]Cl$_2$ (3):** CAUTION! All perchlorate salts in this study should be handled with care because of their potential explosiveness. In a 25 mL round-bottom flask 847 mg bztpen (2.00 mmol) was dissolved in 15 mL MeOH. A solution of 1.03 g Fe(ClO$_4$)$_2$·xH$_2$O (2.00 mmol) in 5 mL MeOH was added dropwise to this mixture. With vigorous stirring, the solution was stirred for 90 min. After 15 min the product was precipitated by adding Et$_2$O to the yellow solution. The crude product was recrystallized in hot MeOH. The yellow crystals were filtered off and dried under vacuum. The obtained crystals were suitable for single crystal X-ray diffraction. The product was obtained as yellow powder (1.10 g, 1.36 mmol, yield 68%). MS (ESI): $m/z = [M+MeO]^+ = 541.22$. Elemental analysis calcld. (%) for C$_{28}$H$_{32}$FeCl$_2$NO$_6$·xH$_2$O: C (46.24, H(4.71), N(9.63). Found: C(46.22), H(4.40), N(9.54).

**Synthesis of perdecanoic acid (PDA):** Synthesized according to literature.\(^{[11]}\) In a 250 mL round-bottom flask 10.0 g decanoic acid (58.1 mmol) were dissolved in 20 mL conc. sulfuric acid (ω = 98%). The mixture was cooled in an ice bath to keep the temperature around 10 °C. Under stirring and proceeding cooling 5 mL of a H$_2$O solution (ω = 50%) was added dropwise over the course of 20 min. The temperature should not rise above 20 °C during the addition. After the addition, the mixture was allowed to stir for another 50 min at 10 °C. The reaction mixture was then slowly diluted with 75 mL ice-cold water, in which the temperature should not rise above 30 °C. The product was extracted five times with 15 mL Et$_2$O using a separatory funnel. The combined organic phase was extracted twice with 15 mL water. The organic phase was dried over Na$_2$SO$_4$ and the filtrate was removed on a rotary evaporator at 25 °C (CAUTION). The colorless residue was dissolved in 100 mL n-hexane and crystallized at −30 °C overnight. The crystals were filtered off and rinsed with cold n-hexane. The product was carefully dried under vacuum. The product was obtained as colorless crystals (6.77 g, 36.0 mmol, yield 62%). $^1$H-NMR (400 MHz, CDCl$_3$, TMS): δ = 11.49 (s br.), 1H, –CO$_2$H), 2.42 (t, 2H, –CH$_2$), 1.70 (quint, 2H, –CH$_2$), 1.40–1.19 (m, 12H, 6 × CH$_2$), 0.88 (t, 3H, –CH$_3$). $^{13}$C-NMR (400 MHz, CDCl$_3$, TMS): $δ = 174.7$ (s, C$_q$), 31.8 (s, –CH$_2$), 30.4 (s, –CH$_2$), 29.3 (s, –CH$_2$), 29.2 (s, –CH$_3$), 29.1 (s, –CH$_3$), 28.9 (s, –CH$_3$), 24.6 (s, –CH$_3$), 22.7 (s, –CH$_3$), 14.1 (s, –CH$_3$). MS (ESI): $m/z = [M+H]^+ = 189.15$. [M + Na]$^+$ = 211.13.

Deposition Numbers 2088337 (for 3), 2088348 (for 1b(ClO$_4$)$_2$), 2088349 (for 1a(BP)$_3$), and 2101789 (for PDA) contain the crystallographic data for this paper. These data are provided free of charge by the Joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

**Acknowledgements**

We gratefully acknowledge support by the Justus-Liebig-Universität Gießen. A.J.A. and D.M. wish to express thanks for the support by the administrators of the JustHPC-cluster of the Justus-Liebig-Universität, Gießen. Open Access funding enabled and organized by Projekt DEAL.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** Iron · Kinetics · Reaction mechanisms · Substituent effects · Time-resolved spectroscopy
L. Duelund, R. Hazell, C. J. McKenzie, L. Preuss Nielsen, H. Toftlund, J. Chem. Soc. Dalton Trans. 2001, 152–156.

[23] a) S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 2011, 32, 1456–1465; b) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104; c) M. Reiher, O. Salomon, B. Artur Hess, Theor. Chem. Acc. 2001, 107, 48–55; d) F. Weigend, M. Häser, H. Patzelte, R. Ahirchrks, Chem. Phys. Lett. 1998, 294, 143–152; e) F. Weigend, R. Ahirchrks, Phys. Chem. Chem. Phys. 2005, 7, 3297–3305; f) K. Eichkorn, F. Weigend, O. Treutler, R. Ahirchrks, Theor. Chem. Acc. 1997, 97, 119–124; g) S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 1980, 58, 1200–1211; h) J. C. Slater, Phys. Rev. 1951, 85, 381–390; i) Proc. R. Soc. Lond. A 1929, 123, 714–733; j) A. D. Becke, J. Chem. Phys. 1993, 98, 5648–5652; k) Lee, Yang. Parr, Phys. Rev. B Condens Matter 1988, 37, 785–789; l) Becke, Phys. Rev. A Gen. Phys. 1988, 38, 3098–3100.

[24] a) Klamt, G. Schüürmann, J. Chem. Soc. Perkin Trans. 2 1993, 799–805; b) A. Schäfer, A. Klamt, D. Sattel, J. C. W. Lohrenz, F. Eckert, Phys. Chem. Chem. Phys. 2000, 2, 2187–2193; c) Perdew, Burke, Ernzerhof, J. Chem. Phys. 1996, 105, 6418–6422; d) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2002, 117, 4729–4737; e) Perdew, Wang, Phys. Rev. B Condens. Matter 1996, 55, 13244–13249; f) P. Deglmann, F. Furche, O. Salomon, M. Reiher, B. A. Hess, J. Phys. Chem. 2002, 106, 7332–7349; g) S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 1980, 58, 1200–1211; h) J. C. Slater, Phys. Rev. 1951, 85, 381–390; i) Proc. R. Soc. Lond. A 1929, 123, 714–733; j) A. D. Becke, J. Chem. Phys. 1993, 98, 5648–5652; k) Lee, Yang. Parr, Phys. Rev. B Condens Matter 1988, 37, 785–789; l) Becke, Phys. Rev. A Gen. Phys. 1988, 38, 3098–3100.

[25] a) Klamt, G. Schüürmann, J. Chem. Soc. Perkin Trans. 2 1993, 799–805; b) A. Schäfer, A. Klamt, D. Sattel, J. C. W. Lohrenz, F. Eckert, Phys. Chem. Chem. Phys. 2000, 2, 2187–2193; c) Perdew, Burke, Ernzerhof, J. Chem. Phys. 1996, 105, 6418–6422; d) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2002, 117, 4729–4737; e) Perdew, Wang, Phys. Rev. B Condens. Matter 1996, 55, 13244–13249; f) P. Deglmann, F. Furche, O. Salomon, M. Reiher, B. A. Hess, J. Phys. Chem. 2002, 106, 7332–7349; g) S. H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 1980, 58, 1200–1211; h) J. C. Slater, Phys. Rev. 1951, 85, 381–390; i) Proc. R. Soc. Lond. A 1929, 123, 714–733; j) A. D. Becke, J. Chem. Phys. 1993, 98, 5648–5652; k) Lee, Yang. Parr, Phys. Rev. B Condens Matter 1988, 37, 785–789; l) Becke, Phys. Rev. A Gen. Phys. 1988, 38, 3098–3100.