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Epoxidation of Olefins Catalyzed by a Molecular Iron *N*-Heterocyclic Carbene Complex: Influence of Reaction Parameters on the Catalytic Activity

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The catalytic epoxidation of olefins by an iron(II) complex bearing a tetradentate bis(pyridyl-*N*-heterocyclic carbene) ligand was investigated. This is the first example of the use of an organometallic iron compound (i.e., with a Fe–C bond) as an olefin epoxidation catalyst. The catalyst system, used without additives, showed good epoxide yields and selectivity for various olefins after a reaction time of 5 min. It was found that the epoxide yield strongly depended on the amount of the peroxide used and its nature and noticeably increased at lower temperatures.

Epoxidation reactions are important transformations of olefins with relevance for both bulk chemical synthesis and the production of fine chemicals and pharmaceuticals.^[1,2] Although a plethora of epoxidation catalysts is known,^[3,4] the need for cheaper and more environmentally friendly epoxidation reactions prevails. The synthesis of iron-based coordination compounds inspired by nature is a promising approach.^[5] In biological systems, enzymes containing active iron sites oxidize a broad range of substrates, including methane. Typical examples are cytochrome P450,^[6] soluble methane monooxygenase,^[7] and Rieske dioxygenases.^[8] Mimicking these biological systems, molecular iron(II) complexes typically involve porphyrin ligand motifs^[9,10] or non-heme N-donor ligands.^[11-17] Valentine et al. was the first to report the epoxidation of olefins with an iron(II) cyclam complex (cyclam = 1,4,8,11-tetraazacyclotetradecane) with very good selectivities towards epoxides.^[11] Other



Scheme 1. Catalytic epoxidation of olefins by using H_2O_2 as the oxidant and the iron(II) complex [Fe(NCCN^{Me})(MeCN)₂](PF₆)₂ (1) as the catalyst.

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ligands such as bpmpn [*N*,*N*'-bis(2-pyridylmethyl)-1,3-diaminopropane] were later used by Que et al. to elucidate the structure–reactivity relationship of aminopyridine ligands in epoxidation catalysis.^[13] In recent catalytic studies, other aminopyridine ligands based on bipiperidine and bipyrrolidine motifs were used with potential applications in asymmetric epoxidation catalysis.^[14, 18, 19]

The groups of Valentine, Nam, and Que analyzed the mechanism of iron(II)-catalyzed epoxidations with hydrogen peroxide.^[11,13,17,20,21] In all cases, the formation of iron(III)–hydroperoxo complexes took place.^[11,22] From this intermediate, a multitude of different reaction pathways for olefin epoxidation and dihydroxylation is possible.^[20,23] A key factor in the mechanism of these conversions is the geometry of the free coordination sites in the ligand sphere. Valentine and Que's research showed that a *cis* conformation of the free bonding sites was of utmost importance to form an iron(V)–oxohydroxo intermediate necessary for dihydroxylation. In contrast, free *trans* coordination sites favored epoxidation reactions.^[11–13,24] Most catalysts with *cis*-labile coordination require acetic acid to work efficiently,^[14,16] and very low epoxide yields are usually obtained under acid-free conditions.^[25–27]

Recent mechanistic investigations showed the formation of a *cis*-bidentate ferric peracetate complex from a catalyst bearing *cis*-labile ligands that went on to form the active iron(V)– oxo oxidant in high yields, which thus explained the increased epoxide yields.^[24,28] This effect was not so pronounced for complexes with *trans* coordination of the solvent molecules,

which are unable to form the *cis*-coordinating ferric peracetate ligand, but they did exhibit good selectivities towards epoxidation without acid additives. Accordingly, new *trans*-labile ligand systems may help to make iron complexes feasible alternatives to wellestablished epoxidation catalysts, such as methyl-trioxorhenium,^[29] Jacobsen's catalyst,^[30] and molybdenum catalysts.^[31]

In this work, the catalytic activity of an iron(II) complex coordinated by the tetradentate di(*o*-imidazol-2ylidenepyridine)methane ligand (in the following denoted as NCCN^{Me})^[32] for the epoxidation of olefins is reported (Scheme 1). To the best of our knowledge, complex 1 is the first organometallic iron complex (i.e., with a direct iron-carbon bond) to be used as an epoxidation catalyst. Complex 1 is stable towards air and water, which is remarkable considering the relative thermodynamic lability of Fe-C compared to Fe-O bonds,^[26] and this renders this system a good candidate for epoxidation reactions.

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First investigations towards the oxidation ability of complex 1 were performed by using *cis*-cyclooctene as the model substrate. Commonly used oxidants such as hydrogen peroxide, *tert*-butyl hydroperoxide (TBHP), and the urea hydrogen peroxide adduct (UHP) were used in these experiments. Alongside these variations, experiments with different catalyst loadings were performed (Table 1).

Table 1. Influence of catalyst loading and oxidant on the conversion of cis-cyclooctene. Conversions were determined by ¹ H NMR spectroscopy by using internal standards.										
Oxidizing agent	Catalyst loading [mol %]	Conv. ^[h] [%] (<i>t</i> [min])	Selectivity ^[h] [%]	Epoxide yield ^[h] [%]	TOF ^[i] [h ⁻¹]					
$H_2O_2^{[a]}$	5 ^[d] 2 ^[e] 1 ^[f] 0.1 ^[g]	99 (5) 92 (5) 66 (5)	> 99 > 99 > 99 > 99	99 92 66	238 552 792					
TBHP ^[b]	2 ^[e]	2 (5) 3 (60)	>99 >99 >99	2 3	480 12 1.5					
UHP ^{ICJ}	2 ^{iej}	12 (5) 14 (60)	>99 >99	12 14	72 7					
Reaction conditions: <i>cis</i> -Cyclooctene (320 µmol, 100 mol%); [a] H_2O_2 (50% aq., 486 µmol), [b] TBHP (70% aqueous, 486 µmol), or [c] UHP (486 µmol); complex 1 ([d] 16 µmol, [e] 6.4 µmol, [f] 3.2 µmol, or [g] 0.32 µmol); $t=5$ min; $T=25$ °C. [h] Conversions and selectivities were determined by ¹ H NMR spectroscopy with benzene as an internal standard [II TOF=enoxide vield/(loading × t)										

Complex 1 was found to selectively catalyze the epoxidation of *cis*-cyclooctene in high yields without the need for acids or other additives within a reaction time of 5 min. The first experiment performed with a catalyst loading of 2 mol% afforded the epoxide in 92% yield after 5 min with no detectable for-

mation of the diol to give a turnover frequency (TOF) of 552 h^{-1} . As expected, increasing the catalyst loading resulted in an increase in the conversion of the olefin. At a catalyst loading of 5 mol%, almost quantitative conversion was observed. Lower catalyst loadings resulted in lower conversions, but high TOFs of up to $792 h^{-1}$ were still maintained. The detection of residual olefin even at 5 mol% catalyst loading might be caused by the limited activity of the catalyst or the fast decomposition of the catalyst under the oxidative conditions. However, the TOFs indicated that limited activity was not a likely factor, as the reaction rates were very high with high conversions after only 5 min.

The reaction was highly sensitive to changes in the oxidizing agent. Whereas aqueous hydrogen peroxide gave the highest conversions of 92% with 2 mol% of 1, the use of other oxidizing agents resulted in significantly lower conversions and 4 to 14% yield. Higher conversions at longer reaction times were only observed for oxidants other than aqueous hydrogen peroxide. With the use of these other oxidants, the reactions were slower and generally showed lower conversions than those obtained with the use of H₂O₂. Reaction times longer than 60 min resulted in no further epoxidation of cis-cyclooctene for all oxidants. The lowered conversions and slower reaction resulting from the use of UHP are readily explained by the fact that the solubility of UHP in acetonitrile is lower than that of aqueous hydrogen peroxide. More interestingly, the conversions were significantly lowered by the use of the alkyl hydroperoxide TBHP. In previous mechanistic work with iron(II) epoxidation catalysts, iron(III)-hydroperoxide complexes were identified as key intermediates towards the active catalysts.^[11,13]

The stability of this intermediate towards decomposition is of high importance to the reaction rate, and the influence of alkyl substituents on the stability of the O-O bond directly affected the rate of the catalytic conversion. Given that the O-O bond is weaker in alkyl hydroperoxides, a shorter lifespan for the iron(III)-hydroperoxo intermediate is reasonable, and this has been shown in other systems.^[11] Several olefin substrates were examined to show the general catalytic activity of complex 1 to epoxidize C=C bonds. The reactions were performed under ambient conditions; conversions and yields were determined by ¹H NMR spectroscopy. Complex 1 was found to efficiently catalyze epoxidation reactions in high selectivities for terminal and cyclic olefins without the need for acids or other additives (Table 2). The TOFs and epoxide yields were highly dependent on the substitution pattern of the double bond in the substrate. However, the selectivities were excellent for the

 Table 2. Epoxidation of various substrates by using complex 1 as a catalyst under ambient conditions. Conversions and selectivities were determined by ¹H NMR spectroscopy by using internal standards.^[a]

Substrate	Catalyst loading [mol%]	Conv. ^[c] [%] (<i>t</i> [min])	Selectivity ^[c] [%]	Epoxide yield [%]	TOF ^[h] [h ⁻¹]
	2	92 (5) ^[d]	>99	92	552
	2	58 (5) ^[d]	>99	58	348
	2	90 (5) ^[e]	>99	90	540
	2	51 (5) ^[e]	>99	51	306
	2	13 (5) ^[e]	84	11	66
	2	18 (5) ^[e]	90	16	96
	1 ^[b]	30 (180) ^[f]	36 ^[g]	11	_[]

[a] Reaction conditions, unless noted otherwise: Olefin (160 µmol, 100 mol%), complex 1 (3.2 µmol), H_2O_2 (50% aq., 243 µmol), t=5 min, T=25 °C. [b] Reaction conditions: Propylene (10.39 mmol, 380 kPa), complex 1 (0.1 mmol), H_2O_2 (50% aq., 15.6 mmol), frozen in liquid N₂ before addition of H_2O_2 then thawed and stirred for 3 h. [c] Conversions and selectivities were determined by ¹H NMR spectroscopy with an internal standard: [d] benzene, [e] pyridine, [f] toluene. [g] 1,2-Propanediol was obtained in 64% yield. [h] TOF=epoxide yield/ (loading_{cat.1}×t). [i] Accurate determination of the TOF was not possible.

formation of epoxides and were largely independent of the substitution pattern of the olefin with the exception of propylene. High epoxide yields were obtained for alkyl-substituted olefins, and the best yields were obtained for cyclic olefins such as cis-cyclooctene, whereas the aromatic olefins styrene and methyl styrene were less prone to epoxidation. This suggested that the nucleophilicity of the olefin was an important factor in the epoxidation and conversely that the catalyst reacted electrophilically. Rybak-Akimova showed that this effect correlates well with the oxidation potential of the substituted olefins. $^{\left[14,33\right] }$ In other reports on epoxidation catalysis with iron(II) aminopyridine complexes, cyclic olefins were proven to give significantly higher yields for epoxidations and dihydroxylations than terminal olefins.^[11, 14, 25] In none of these studies was propylene examined; however, it is known from other homogeneous systems that propylene epoxidation is still a challenge with most catalysts and that only low or moderate epoxide yields^[29, 34, 35] are obtained with only a few exceptions.^[36] Propylene epoxidation with complex 1 afforded moderate conversions, which proved its activity towards unactivated olefins.

Given that in all previous experiments no quantitative conversion of the olefin was achieved, the influence of the concentration of hydrogen peroxide on the conversion was investigated (compare Figure 1). During the fast catalytic conver-



Figure 1. Conversion of *cis*-cyclooctene dependent on the number of equivalents of the oxidant. Reaction conditions: *cis*-Cyclooctene (320 µmol, 100 mol%), complex 1 (6.4 µmol, 2 mol%), H₂O₂ (varying equiv., 50% aq.), t=5 min, T=25 °C.

sion, gas evolution from the reaction solution was observed, which indicated that unproductive hydrogen peroxide decomposition might have occurred, catalyzed by complex 1, as it is well known for other iron(II) compounds.^[37,38] If less than 150 equivalents H_2O_2 was used, the conversion was lower than that expected for complete conversion of the oxidant.

In the range from 150 to 300 equivalents H_2O_2 , maximum conversions were reached. At higher oxidant concentrations, the conversions decreased again. The conversions for low H_2O_2 concentrations and the observed evolution of gas during the reaction suggested that some of the oxidant decomposed and thus could not productively react to the epoxide. Under these

conditions, hydrogen peroxide was the limiting reagent in the epoxidation reaction.

At higher concentrations, this could not be the case, as there was a certain amount of H_2O_2 left after the reaction time, as indicated by a violent reaction with activated MnO_2 . It is more probable that the activity of the complex was lowered as a result of partial deactivation of the iron catalyst.

If the concentration of hydrogen peroxide was a limiting factor after the reaction was finished, there would still be active catalyst present in the reaction mixture. Two control experiments were conducted to investigate the catalyst stability towards oxidants in the presence of an excess amount of the substrate. In the first experiment, 150 equivalents H_2O_2 was used with 100 equivalents substrate and 2 equivalents catalyst. After incomplete conversion in 5 min, another 150 equivalents H₂O₂ was added, which resulted in no further catalytic conversion. In the reciprocal case of 50 equivalents H₂O₂ with another 50 equivalents added after 5 min, a conversion of 83% was reached, which showed that the complex was still active in the presence of an excess amount of the substrate after a first reaction cycle. Even if 24 h passed before the second addition, the conversion reached 72%. This indicated that the catalyst had decomposed only to a slight degree and showed that the catalyst was remarkably stable in the presence of an excess amount of the substrate. In principle, this renders the catalyst recyclable, as it retains most of its activity as long as there is an excess amount of the substrate. Ligand design to facilitate recycling and enhance stability towards oxidants therefore seems worthwhile and investigations are currently underway.

Kinetic studies showed that at room temperature the catalytic conversion was complete after 2 min (Figure 2). As expected, the overall activity of the catalyst was lowered at decreased temperatures. The initial TOF at room temperature determined by the initial slope was very high at 2624 h^{-1} , which corresponded to 87% conversion after a reaction time of just 1 min. However, the epoxidation did not proceed to more than 90% conversion, which corresponded to a negligible increase in the



Figure 2. Effect of lowering the temperature in the catalytic oxidation of *cis*-cyclooctene. Reaction conditions: *cis*-Cyclooctene (319 µmol, 100 mol%), complex 1 (6.4 µmol, 2 mol%), and H_2O_2 (50% aq., 486 µmol, 150 mol%), T = -10 (**n**), 0 (**o**), 10 (**A**), and 25 °C (**V**).

turnovers after the initial phase of a high TOF. This complied with all our previous experiments with H_2O_2 in which conversions at room temperature were recorded after 5 min with no further reaction after this short reaction period (Tables 1 and 2). At a reaction temperature of 10 °C, the TOF was lower (1437 h⁻¹), which corresponded to a conversion of 96% after 2 min. At 0 and -10 °C, the TOF was 568 and 368 h⁻¹, respectively, with a maximum conversion of 99% at 0 °C and 100% at -10 °C.

In general, for these kinetic experiments the maximum conversions were increased at lower temperatures, whereas the TOFs of the catalyst were lowered. A viable explanation for this behavior is the combined influence of the temperature on the stability and activity of the catalyst. Whereas compound **1** reacted to the catalytically active species under oxidative conditions, deactivation of the catalyst was also observed (see Scheme 1). Both of these pathways were slowed down at decreased temperatures; however, the unproductive decomposition pathway was slowed down to a greater extent than the productive epoxidation pathway. The resulting increased period of activity of the catalyst resulted in increased conversions up to total conversion of 100% even though the activity itself was lowered. Overall, the increased maximum conversion is therefore a stability effect rather than an activity effect.

Generally, a comparison of literature-reported TOFs was somewhat problematic owing to the varying reaction conditions and, more importantly, to the great variation of sampling times and reaction times within the data. The highest TOF of 25 200 h⁻¹ corresponding to 50% yield of cyclooctene oxide with 0.5 mol% catalyst after 14 s was reported by Que et al. for the non-heme iron epoxidation catalyst [(bpmen)Fe(MeCN)₂]²⁺ .^[20] However, this result was only obtained in the presence of additives. Under additive-free conditions, the highest reported value was approximately 4080 h⁻¹, which corresponded to a 17% yield after 30 s.^[20] Although there are a few reports on reactions with additives with TOFs exceeding 1000 h^{-1,[14]} most systems usually have (maximum) TOFs of 100–1000 h^{-1,[15,24]} This comparison highlights the good performance of iron *N*heterocyclic carbene complexes in epoxidation reactions.

In summary, the application of the first organometallic (i.e., with a Fe-C bond) iron complex for olefin epoxidation was reported. This catalyst was quite active for a broad range of olefins with moderate to high selectivity. To find the optimal reaction conditions, the epoxidation of cis-cyclooctene was investigated in detail; hydrogen peroxide was the most efficient oxidant. Changing the concentration of H₂O₂ showed that the oxidation agent was only the limiting reagent if used in lower (equivalent) amounts, whereas a large excess amount of the oxidant favored decomposition of the catalyst. A second addition of the oxidant demonstrated that the catalyst remained active if an excess amount of the substrate was present. The highest obtained TOF for this system so far was approximately 2600 h⁻¹. Further studies with regard to the characterization of the reactive intermediates and ligand design to enhance stability and activity are currently under investigation in our laboratories.

Experimental Section

General methods

Complex 1 was synthesized according to a literature procedure.^[32] Unless otherwise noted, all conversions were determined by calibrated GC analysis by using *p*-xylene as an internal standard. Experiments performed by using different substrates were analyzed by ¹H NMR spectroscopy for which the specific product signal integrals were compared to the internal standard used.

Catalytic epoxidation of cis-cyclooctene

General procedure: *cis*-Cyclooctene (35.2 mg, 319 µmol) was added to a vial charged with a solution of complex **1** (5 mg, 6.4 µmol) in acetonitrile (1 mL). A solution of H₂O₂ (50% in H₂O, 27.6 µL, 486 µmol) in acetonitrile (1 mL) was then added. The reaction mixture was stirred for 5 min and activated MnO₂ was added to terminate the reaction. After filtration, GC samples were prepared by diluting a portion of the reaction mixture (100 µL) with *n*-hexane (900 µL) and the GC standard (4 mgmL⁻¹ *p*-xylene in *i*PrOH, 500 µL). ¹H NMR spectroscopy experiments were conducted in CD₃CN. After 5 min of stirring, the internal standard was added, the catalyst was removed by adsorption to alumina, and the ¹H NMR spectra were recorded.

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