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Transition metal mediated oxygen transfer to organo nitrogen compounds

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Contents

Abstract

The oxidation of organo nitrogen compounds opens up an access to a multitude of versatile building blocks for organic synthesis. In the past, the synthetic benefit of these reactions was often reduced by a lack of selectivity. During the last few decades, transition metal mediated oxygen transfer reactions—either stoichiometric or catalytic—helped to overcome this dilemma. This review will summarize recent developments in the synthetic chemistry related with *N*-oxidations as well as recent mechanistic insights.

Keywords: Organo nitrogen compounds; Oxidation; Reaction mechanisms

1. Introduction

Transition metal mediated/catalyzed oxidations and reductions are of general relevance for synthetic organic chemistry. Such transformations are mainly carried out at carbon atoms but are also known for nitrogen, silicon, phosphorus and sulfur.

Purely inorganic nitrogen compounds occupy stable formal oxidation states from −III (NH_3) to + V (NO_3^-). The catalytic reduction of N_2 to NH_3 (Haber-Bosch Process) and the catalytic oxidation of NH_3 to NO (Ostwald Process)—the precursor of HNO_3 and nitrates—have become milestones for the development of industrialized societies.

In organic chemistry, a broad range of differently oxidized nitrogen centers is known as well, with amines and nitro derivatives being found at the top and the bottom of the scale. Since amino and nitro groups can be introduced into organic fragments by simple procedures such as nucleophilic aliphatic/aromatic substitution or electrophilic aromatic substitution, there is a demand for selective pathways to compounds bearing nitrogen moieties in intermediate oxidation states. This review will mainly focus on *oxidation* reactions at organo nitrogen centers by *oxygen transfer*. Since, in contrast to the synthetic benefit of selective oxidations of organic nitrogen compounds, there is only little understanding about mechanistic details of such reactions up to now, these aspects will claim an important part of the following discussions. Beside classical oxygen transfer reactions, organic nitrogen compounds undergo a series of other oxidations like diazotations, radical type reactions,

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dehydrogenations, oxidative aminations, nitrosations, nitrations, halogenation, etc. which will be mentioned only in passing.

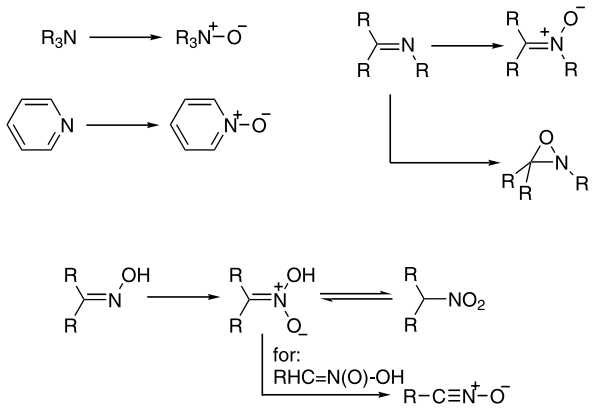
2. The oxidation of organo nitrogen derivatives — an overview

First a short overview over the quite complex oxidation chemistry of organo nitrogen compounds shall be given. In this context it should be mentioned, that for most of the conversions discussed below the reductive back reactions are known.

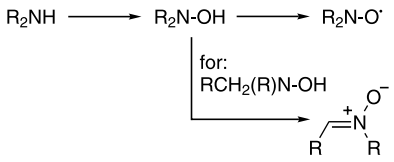
Oxygen transfer to tertiary amines as well as to aromatic nitrogen compounds with the nitrogen atom being part of the aromatic ring system leads to the formation of *N*-oxides (Scheme 1). Nitrones, which can be considered as the *N*-oxides of imines, are thus available by *N*-oxidation of these unsaturated compounds.

If the oxidizing agent will not attack at the nitrogen but at the carbon atom of the C=N moiety, oxaziridines are formed, which are versatile oxygen transfer agents themselves. Oximes can be *N*-oxidized to nitroxides, tautomers of nitro compounds. If the oximes possess an α-hydrogen atom, nitrile oxides are obtained, which undergo cyclization with C–C multiple bonds.

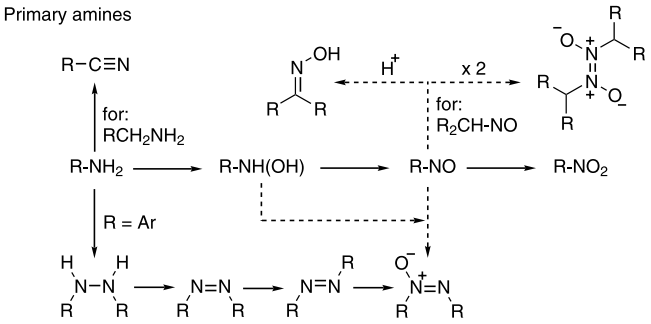
During the oxidation of secondary amines (Scheme 2) secondary hydroxylamines are formed first, which can be oxidized to nitroxides in the absence of an α-CH group. Otherwise further oxidation followed by the elimination of water generates nitrones. These can undergo hydrolysis to aldehydes RCHO and primary hydroxylamines (not shown in Scheme 2).



Scheme 1.



Scheme 2.



Scheme 3.

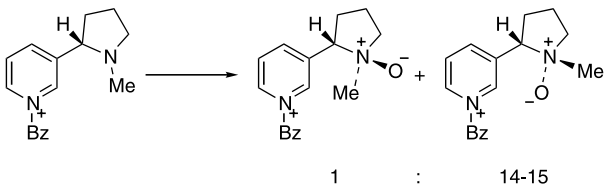
The main oxidation pathways of primary amines are summarized in Scheme 3. Hydroxylamines and nitroso derivatives are known as the intermediates of the direct oxidation to nitro compounds. Depending on the nature of the substituent R different pathways and side reactions are possible: aromatic primary amines can be converted in a radical reaction via 1,2-diarylhydrazines to azo compounds, which can be oxidized subsequently to the corresponding azoxy derivatives. These systems are alternatively accessible via condensation (dashed lines) of hydroxylamines and nitroso compounds. Aliphatic primary amines of the type $R_2CH–NH_2$ give the corresponding nitroso compounds $R_2CH–NO$ which can dimerize before undergoing further oxidation or rearrange to oximes in the presence of an acid. Aliphatic primary amines of the type $RCH_2–NH_2$ can also be oxidized to yield the nitriles RCN.

For many of the reactions described above, peroxidic compounds like peracids or hydrogen peroxide are the oxygen transfer agents of choice. This opens up the door to transition metal catalysis, since a multitude of homogeneous and heterogeneous transition metal compounds have found to activate peroxidic compounds in the past. Other *N*-oxidations involve electron transfer reactions, which also include transition metal complexes as catalysts or stoichiometric reagents.

3. Oxygen transfer to tertiary nitrogen atoms

Organic compounds with tertiary nitrogen atoms give the corresponding *N*-oxides by treatment with peroxidic reagents. Hydrogen peroxide is the reagent of choice in these cases. In a theoretical study it was proved, that the reaction follows a concerted mechanism [1]. Depending on the electronic situation of the substrate, activation of the oxidizing agent is required. This is possible by the in situ formation of peracids, [2] the application of a commercially available peracid like *m*-CPBA [3], of $KHSO_5$ [4], of oxaziridines or dioxiranes [5]. More powerful oxygen transfer agents for the formation of *N*-oxides are HOF and ozone, [6] asymmetric *N*-oxidation is possible by enzymatic protocols [7].

A whole series of vanadium, molybdenum and tungsten compounds have shown to be suitable catalysts for the



Scheme 4.

activation of hydrogen peroxide or organic peroxides for oxygen transfer to tertiary amines [8]. This was used e.g., for the oxidation of 1-benzylnicotinium bromide giving the corresponding *N*-oxides with diastereomeric excesses of 1:14–15 (Scheme 4) [9].

N-Oxides have found to be versatile ligands for transition and lanthanoid/actinoid metals. For this purpose a series of derivatives of 2-phosphinylpyridine-*N*-oxide was synthesized using hydrogen peroxide as the oxygen source [10]. *N*,*N*-Dialkyl anilines require more drastic conditions than pyridines for *N*-oxidation. 2-Diphenylphosphinoyl-*N*,*N*-dimethyl aniline is *N*-oxidized by hydrogen peroxide in the presence of $MoO(O_2)_2{\cdot}(H_2O)_x$ [11]. This directly leads to the corresponding molybdenum peroxo complex $MoO(O_2)_2{\cdot}(Ph_2PC_5H_4N(O)Me_2)$ shown in Fig. 1.

Using the combination of ^{t}BuOOH/*L*-(+)-(diisopropyltartrate)/Ti(^{i}PrO)$_4$, well known from the enantioselective epoxidation of allylic alcohols, it was possible to perform a kinetic resolution of racemic β-hydroxy amines by *N*-oxide formation (Scheme 5) [12].

A very efficient method for the generation of pyridine *N*-oxides was found by Sharpless et al. who used bis(trimethylsilyl) peroxide in the presence of catalytic amounts of inorganic rhenium compounds as the oxidizing agent [13]. Additionally, some routes to *N*-oxides based on ruthenium and manganese catalysts have been published [14].

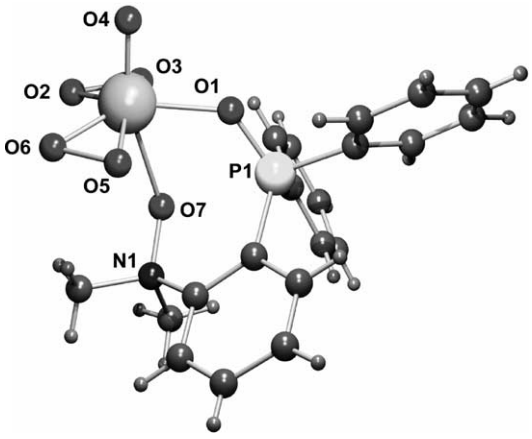
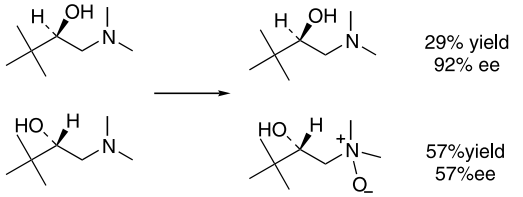


Fig. 1. Solid state structure of $MoO(O_2)_2{\cdot}(Ph_2PC_5H_4N(O)Me_2)$.



Scheme 5.

4. Synthesis of nitrones, oxaziridines and nitroxides

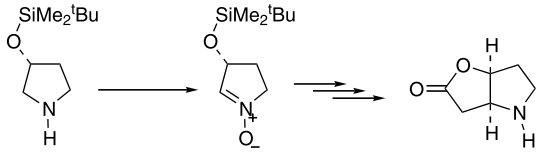
Imines are easily obtained by condensation of aldehydes/ketones and amines. However, ruthenium catalyzed oxidation of secondary amines, probably occurring at one of the α-carbon atoms, has opened up on new access to this class of compounds [15]. Imines can be oxidized to the corresponding nitrones by using percarboxylic acids [16], dioxiranes [17] or oxaziridinium salts [18]. There is one example for the oxidation of imines to nitrones with $KMnO_4$ as the oxidizing agent [19]. Depending on the substitution pattern of the substrate, [20] oxaziridines are obtained by oxidation of imines with peracids [21] or hydrogenperoxide in the presence of a base [22] or a nitrile [23].

The most simple route to nitrones is the oxidation of amines or hydroxylamines. In general percarboxylic acids are applied as oxygen transfer agents, [24] but the usage of ^{t}BuOOH [25], NaOCl [26] and dioxiranes [27] has also been published.

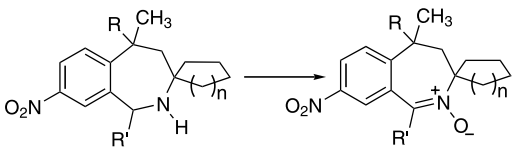
A whole variety of high valent transition metal compounds like MnO_2, $(NPr_4)RuO_4$ or Ag_2O have been used as stoichiometric reagents for the oxidation of hydroxylamines to nitrones during the last years [28]. These systems were investigated mainly to replace HgO, an environmentally quite unfavorable but highly efficient reagent for this reaction [29].

However, catalytic oxidation of secondary amines or hydroxylamines with active oxygen compounds will be the first choice for the generation of nitrones in the future. Just a few examples where heterogeneous catalysts were applied have been published up to now. TS-1 is an efficient catalyst for the oxidation of secondary amines to nitrones with hydrogen peroxide as the oxidizing agent, in some cases, hydroxyl amines can be isolated [30].

Homogeneous catalysts mainly requires Lewis-acidic, high valent group VI and VII complexes as the catalytically active species. Tungsten complexes have especially shown good activities in the transformation of secondary amines to nitrones by hydrogen peroxide [31]. This method as also been applied for intermediate steps in the synthesis of natural products like the Geissman-Waiss lactone (Scheme 6) [32] or optically active precursors of pyrrolidine alkaloids [33].



Scheme 6.



Scheme 7.

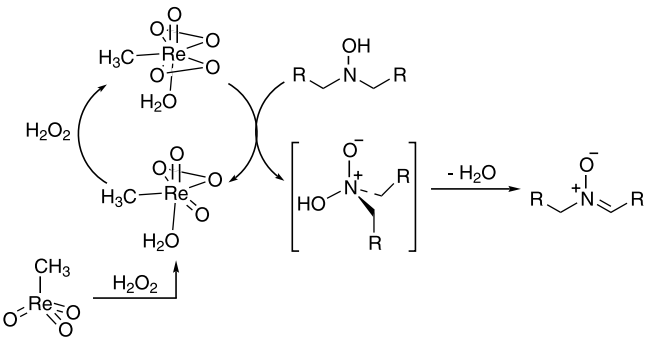
Even sterically hindered spirocyclic nitrones derived from 8-nitro-1,2,4,5-tetrahydro-3H-spiro[2-benzazepin-3,1′-cycloalkanes] can be obtained following this procedure (Scheme 7) [34].

Hydrogen peroxide can also be activated by CH_3ReO_3 for the oxidation of secondary amines and hydroxylamines giving nitrones in excellent yields [35]. In a detailed mechanistic study, Espenson et al. investigated the mechanism of the oxygen transfer to secondary hydroxylamines. In the presence of an excess of hydrogen peroxide, the actual oxygen transferring agent $CH_3ReO(O_2)_2$ is generated by perhydrolysis of CH_3ReO_3 (Scheme 8) [36]. The kinetic data they obtained make the intermediate formation of a hydroxylamine *N*-oxide favorable, which will eliminate water to give the nitrone. Two products are formed from unsymmetrical hydroxylamines (R≠R′), the ratio of which establishes the reactivities of the intermediate toward the competing elimination reactions:

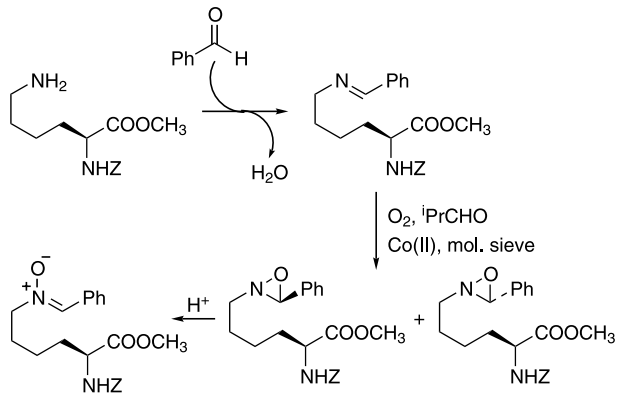
$$(RCH_2)(R'CH_2)NOH \rightarrow (RCH_2)(R'CH_2)N(O)OH \rightarrow$$
$$RCH_2N(O){=}CHR' + R'CH_2N(O){=}CHR$$

Jacobsen's catalyst, a Mn(III) salen complex, oxidizes secondary hydroxyl amines cleanly to the corresponding nitrones with hydrogen peroxide, sodium hypochlorite or iodosylbenzene as the oxygen source [37]. With *meso-cis*-3,4-isopropylidenedioxy-1-hydroxypyrrolidine an enantiomeric enrichment in the product up to 36% ee was observed.

The coordination chemistry of nitroxides, paramagmnetic compounds of high stability, with transition metal centers is of interest due to some special magnetic properties of such complexes. Despite the fact that nitrones are closely related to nitroxides, there are just a few reports on the coordination chemistry of nitrones, which seem to form quite



Scheme 8.



Scheme 9.

stable complexes with a whole variety of transition metal fragments [38].

Some reports on the metal catalyzed oxidation of imines to oxaziridines have been published up to now. Investigations of Tolstikov et al. in the early seventies proved, that group VI compounds like $MoCl_5$ or $Mo(CO)_6$ can activate ^{t}AmylOOH for oxygen transfer to imines giving oxaziridines in high yields [39]. In 1995, Jørgensen et al. reported, that oxaziridines can be synthesized from imines by the combination of dioxygen, an aliphatic aldehyde and some cobalt complexes [40]. Probably a peracid, Co-catalyzed formed from the aldehyde and dioxygen, is the oxygen transferring agent, as it is known from the so-called Mukayama olefin epoxidation and Baeyer-Villiger oxidations. This method was recently applied for the synthesis of an oxaziridine derived from the amino acid lysine by Miller and coworkers [41] (Scheme 9). The product can be isomerized to the corresponding nitrone under protic conditions, both compounds are precursors for the synthesis of microbial iron(III) chelating siderophores.

Nitroxides $RN(O^{\bullet})R'$ are formed by the oxidation of secondary amines $RN(H)R'$ via the corresponding secondary hydroxylamines $RN(OH)R'$, in the absence of α-hydrogen atoms in the groups R and R′. Depending on the structure of the system, stable radicals can be obtained, which have gained applications as spin traps, organic magnets or as starters for (living) radical polymerizations. Usually, the oxidation is performed by percarboxylic acids like MCPBA [42]. These reagents can be replaced by high valent (transition) metal compounds like MnO_2, Ag_2O or PbO_2 [43].

5. The oxidation of primary amines

As already depicted in Scheme 3, the oxidation of primary amines may lead to a whole variety of different products. The development of selective pathways is therefore the central point in this chemistry.

In a straight forward reaction nitro compounds can be obtained directly from primary amines. This conversion requires three oxygen atoms per nitrogen atom to be

transferred: $RNH_2+3^tBuOOH \rightarrow RNO_2+3^tBuOH+H_2O$. If a three step pathway is postulated, at least two intermediates—hydroxylamines and nitroso compounds—should occur. These intermediates can be isolated depending on the chemical structures of the substrates and the oxidizing agents applied.

From a synthetic point of view, hydroxylamines are difficult to obtain. They are easily oxidized further or undergo condensation reactions. There are electronic reasons for this behavior as described later. Recently, a protocol using $KHSO_5$ over silica gel or alumina has been published, which enables the synthesis of hydroxylamines derived from primary and secondary amines in high yields [44]. Additionally dioxiranes are suitable oxidizing agents for this reaction [45]. Transition metal based oxidations of primary amines to hydroxylamines have not been reported so far, probably due to over oxidation of the sensitive hydroxylamine moiety giving nitroso or nitro compounds.

For the synthesis of nitroso derivatives from primary amines, dimethyl dioxirane, per carboxylic acids, oxaziridinium salts or DDQ have been used as organic reagents [18,46]. Sodium perborate and percarbonate oxidize primary aliphatic amines to aliphatic nitroso compounds in good to excellent yields [47]. However, compared to hydroxylamines, nitroso compounds have a reduced reactivity towards oxidizing compounds. This allows transition metal compounds to be introduced in the synthesis of these interesting systems. Therefore some catalytic routes to aromatic nitroso derivatives have been worked out during the last years.

Espenson et al. have used H_2O_2 in the presence of methylrhenium trioxide for this reaction and have investigated the mechanism in a detailed kinetic study. For 4-substituted *N*,*N*-dimethylanilines, which give the *N*-oxide as the only product [48], they found that the oxidation is inhibited by electron-withdrawing substituents in the 4-position following a linear Hammett relationship. Interestingly, aniline is oxidized by a factor of 10 slower than *N*,*N*-dimethylaniline while *N*-phenylhydroxylamine is oxidized by a factor of 90 faster than its precursor aniline, demonstrating the high activity of primary hydroxylamines towards peroxidic agents.

Almost parallel to these investigations, Krohn et al. established the zirconium catalyzed oxidation of primary anilines with ^{t}BuOOH as the oxygen source [49]. Usually, the reaction leads directly to the corresponding nitro derivatives but with electron rich anilines, up to 40% of the related nitroso compound can be obtained. The authors could prove hydoxylamines occurring as intermediates due to the formation of minor amounts of azoxy compounds, the condensation products of hydroxylamines and nitroso compounds (see Scheme 3) [50].

Most of the work on the oxidation of primary aromatic amines to the corresponding nitroso derivatives has been done with group VI metal complexes. $Na_2MoO_4\cdot(H_2O)_2$, $(n\text{Bu}_4\text{N})_4\text{Mo}_8\text{O}_{26}$, *cis*-$Mo(O)_2(acac)_2$ and $Na_2MoO_4\cdot(H_2O)_2$ have found to be able to activate hydrogen peroxide for this reaction [51]. Due to the mild conditions, the desired aromatic nitroso compounds are obtained in high yields.

The selective oxidation of amines to nitro compounds requires more drastic conditions than the oxidations discussed before and therefore highly reactive oxidizing agents. During the last years dimethyl dioxirane, either isolated in acetone solution or generated in situ from $KHSO_5$ and acetone, and HOF-generated from fluorine and water—in acetonitrile turned out to be the reagents of choice [52,53]. Before, sodium percarbonate, ozone and percarboxylic acids were applied [54].

Transition metal compounds can fulfil the demands for this oxidation reaction by different mechanisms: a high oxidation potential which is closely related to a high oxidation state especially for vanadium, chromium and group VII to XI metals will give rise to radical type oxidations of the amine, which finally may lead to the corresponding nitro compounds. There are some examples for this kind of reactivity, like chromium exchanged silicalites with ^{t}BuOOH as the oxidizing agent or $RuCl_3$ and hydrogen peroxide [55]. Secondly, reacting Fe(III) or Mn(III) porphyrins with PhIO or ^{t}BuOOH gives rise to the formation of high valent oxo species which are also capable of oxidizing nitroso compounds to the corresponding nitro compounds [56]. A third type of reactivity is based on the Lewis acidity of early transition metals centers in high but nevertheless stable oxidation states. These species are able to activate peroxidic agents like hydrogen peroxide or ^{t}BuOOH for the oxygen transfer without changing their oxidation states. Therefore radical type side reactions are suppressed. Classical examples are the methyltrioxorhenium/hydrogen peroxide system, which catalyzes the oxidation of organonitrogen compounds as found for dimethyl dioxirane, or Na_2WO_4/hydrogen peroxide, which has been applied for the oxidation of 3-nitro-1,2,4-triazoles [57]. Probably the best system for the oxidation of primary aromatic and aliphatic amines to nitro compounds has been developed by Krohn et al. during the late 90s [49].

Depending on the organic substituent at nitrogen, the catalyst $Zr(O^tBu)_4$ gives yields of nitro compounds up to 98% with ^{t}BuOOH as the oxygen source. As already depicted above, electron deficient aromatic amines like 4-nitroaniline are oxidized rapidly to the corresponding nitro compounds while for electron rich systems like 4-methoxyaniline, the final oxidation from the nitroso to the nitro product is slow [49]. This is due to a fundamental decrease of the electron density at the nitrogen atom with the progressive oxidation.

With these results in mind, a detailed quantum chemical study on mechanistic aspects of this reaction was carried out [58]. Since $Zr(O^tBu)_4$ (in combination with ^{t}BuOOH) is the best catalyst for this reaction, obviously due to the bulky $^tBuO^-$ ligands which prevent the oligomerization of the active sites via alkoxide bridges, the hypothetical monomeric $Zr(OMe)_4$ (**1**) was used as the model catalyst, $MeNH_2$ as the substrate, and MeOOH as the oxidizing agent.

The activation of ROOH at Zr(IV) should mechanistically be related to the activation of peroxides at titanium (Sharpless epoxidation) or molybdenum (epoxidation of unfunctionalized olefins) catalysts [59]. At M-OR or $M(O_2)$ fragments, ligand exchange can occur, generating η^2 co-ordinated ROO^- ligands. This was calculated to be slightly exothermic for the reactions xMeOOH+Zr(OMe)$_4$ (**1**)→Zr(OMe)$_x$(OOMe)$_{4-x}$+xMeOH ($x=0$–3; ΔH_R: −2.3 to −7.3 kcal mol^{-1}), but endothermic for the reaction ^{t}BuOOH+Zr(O^{t}Bu)$_4$→Zr(O^{t}Bu)$_3$(OO^{t}Bu)+^{t}BuOH (ΔH_R: +10.8 kcal mol^{-1}). Therefore Zr(OMe)$_3$(OOMe) (**2**, Fig. 2) was chosen as the activated intermediate for oxygen transfer to $MeNH_2$.

Since amines are known to co-ordinate to zirconium alcoholates, the complexation of Zr(OMe)$_4$ (**1**) and Zr(OMe)$_3$(OOMe) (**2**) with methyl amine was calculated giving the trigonal bipyramidal zirconium species Zr(OMe)$_4$(MeNH$_2$) (**3**; ΔH_R: −12.3 kcal mol^{-1}) and Zr(OMe)$_3$(OOMe)(MeNH$_2$) (**4**; ΔH_R: −15.8 kcal mol^{-1}) with the amino ligand co-ordinated in the axial position.

An exchange of a MeO^- by a $MeHN^-$ ligand would increase the nucleophilicity and therefore the activity of the substrate. Aminolysis and subsequent loss of methanol (Fig. 2) of Zr(OMe)$_4$(*ax*-NH$_2$Me) (**3**) and Zr(OMe)$_3$(OOMe)(*ax*-NH$_2$Me) (**4**) leads to Zr(OMe)$_3$(NHMe) (**5**; ΔH_R: +30.9 kcal mol^{-1} relative to **3**) and Zr(OMe)$_2$(OOMe)(NHMe) (**6**; ΔH_R: +31.6 kcal mol^{-1} relative to **4**). The high endothermicity agrees with the reactivity of metal amides giving alcoholates when treated with alcohols [60]. Nevertheless, an amide pathway was also included in the calculations on the oxygen transfer processes.

The uncatalyzed oxidation of $MeNH_2$ by MeOOH leads to methylamine *N*-oxide and MeOH. Therefore an oxygen atom and a proton must be transferred parallely. This is revealed by the geometry of the transition state **Ox1** (Fig. 2; $\Delta H^{\#}$: +35.0 kcal mol^{-1}): the lone pair of the nitrogen is atom attacked electrophilically by the oxenoid oxygen atom of MeOOH, while the proton bridges the O–O unit. The resulting *N*-oxide (ΔH_R: +0.5 kcal mol^{-1}) is not the final product of this reaction. It tautomerizes to *N*-methyl hydroxylamine (ΔH_R: −21.3 kcal mol^{-1}).

Two different pathways were calculated for the metal catalyzed oxygen transfer. The amine adduct **4** leads to transition state **Ox1^{Zr}** ($\Delta H^{\#}$: +22.0 kcal mol^{-1} relative to **4**) wherein the amine is no longer co-ordinated to the zirconium atom but fixed to the active site by a NH···OMe hydrogen bond. Oxygen transfer results in the formation of Zr(OMe)$_4$(*O*NH$_2$Me) with the *N*-oxide co-ordinating to zirconium by the oxygen atom. Like in the uncatalyzed reaction a proton shift gives the more stable tautomer Zr(OMe)$_4$(HO*N*HMe) (**7**) wherein the nitrogen atom of *N*-methyl hydroxylamine co-ordinates to zirconium. The co-ordination geometry at the nitrogen atom in **Ox1^{Zr}** very

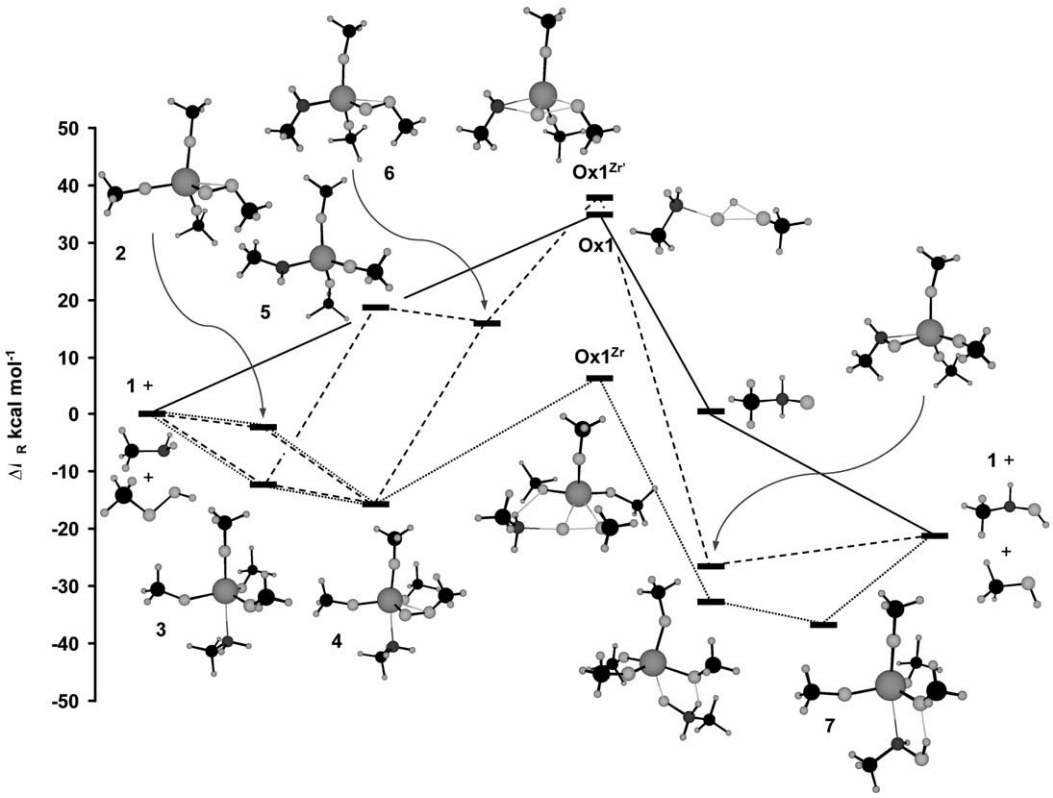


Fig. 2. Calculated pathways for the oxidation of $MeNH_2$ to MeNH(OH); —, uncatalyzed reaction; . . . , catalyzed reaction without zirconium amide intermediate; ---, catalyzed reaction with zirconium amide intermediate.

much resembles the geometry of **Ox1** and clearly proves an electrophilic attack at the nitrogen lone pair.

As mentioned above, the second metal catalyzed pathway includes a strongly endothermic preaminolysis generating **6** from **4**. The activation barrier for the oxygen transfer related to $\mathbf{Ox1}^{\mathbf{Zr'}}$ ($\Delta H^{\#}$: + 37.9 kcal mol^{-1} relative to **1**) was calculated to be even higher than the barrier of the uncatalyzed reaction. This may be due to a strong bending of the N–O–O fragment in the transition state.

The transition state **Ox2** of the uncatalyzed oxidation of MeNH(OH) very much resembles **Ox1** (oxygen transfer to $MeNH_2$). An enthalpy of activation of + 31.1 kcal mol^{-1} was calculated for this reaction. The reaction does not stop with the *N*-oxide but proceeds via *N*-methyl dihydroxylamine (tautomerization) to nitrosomethane (water elimination) as shown in Fig. 3.

For the zirconium catalyzed reaction, again two pathways (without or with amide formation) were calculated. Co-ordination of *N*-methyl hydroxylamine to $Zr(OMe)_4$ gives complex $Zr(OMe)_4$(HO*N*HMe) (**7**) in an exothermic reaction which is in equilibrium with $Zr(OMe)_3$(OOMe)(HO*N*HMe) (**8**) when MeOOH is present. In the transition state $\mathbf{Ox2}^{\mathbf{Zr}}$ ($\Delta H^{\#}$: + 18.2 kcal mol^{-1} relative to **8**) the MeNH(OH) ligand is decoordinated from zirconium, but linked to the active site by a hydrogen bond. After the oxygen transfer, a zirconium complex of *N*-methyl hydroxylamine *N*-oxide is obtained, wherein the oxygen atom of the N=O unit co-ordinates to the transition metal. In a series of reactions, nitroso methane is released as the final product.

Including the formation of an amide involves a strongly endothermic aminolysis of $Zr(OMe)_4$ or $Zr(OMe)_3$(OOMe) with *N*-methyl hydroxylamine as the amine component and finally leads via **9** to $Zr(OMe)_2$(OOMe)(*N*MeOH) (**10**). The geometry of the transition state $\mathbf{Ox2}^{\mathbf{Zr'}}$ of the following oxygen transfer step ($\Delta H^{\#}$: + 37.5 kcal mol^{-1} relative to **1**) is analogous to $\mathbf{Ox1}^{\mathbf{Zr'}}$. The oxidation gives a zirconium complex with a mono deprotonated η^2 co-ordinating *N*-methyl dihydroxylamino ligand, from where MeNO is liberated in a series of subsequent reactions.

The nitrogen atom is the only site for oxygen transfer to MeNO. For the uncatalyzed reaction (transition state **Ox3**) a reduced barrier of activation ($\Delta H^{\#}$: + 24.0 kcal mol^{-1}; 35.0 kcal mol^{-1} for **Ox1** and 31.1 kcal mol^{-1} for **Ox2**) was found (Fig. 4). This correlates with a complete change in the electronic situation: $MeNH_2$ and MeNH(OH) have been negatively polarized substrates (Mullikan charges: −0.625 and −0.264 at nitrogen). In contrast, MeNO carries a positive charge (+0.077) at nitrogen. Therefore MeNO does not react as a nucleo- but as an electrophile, which influences the

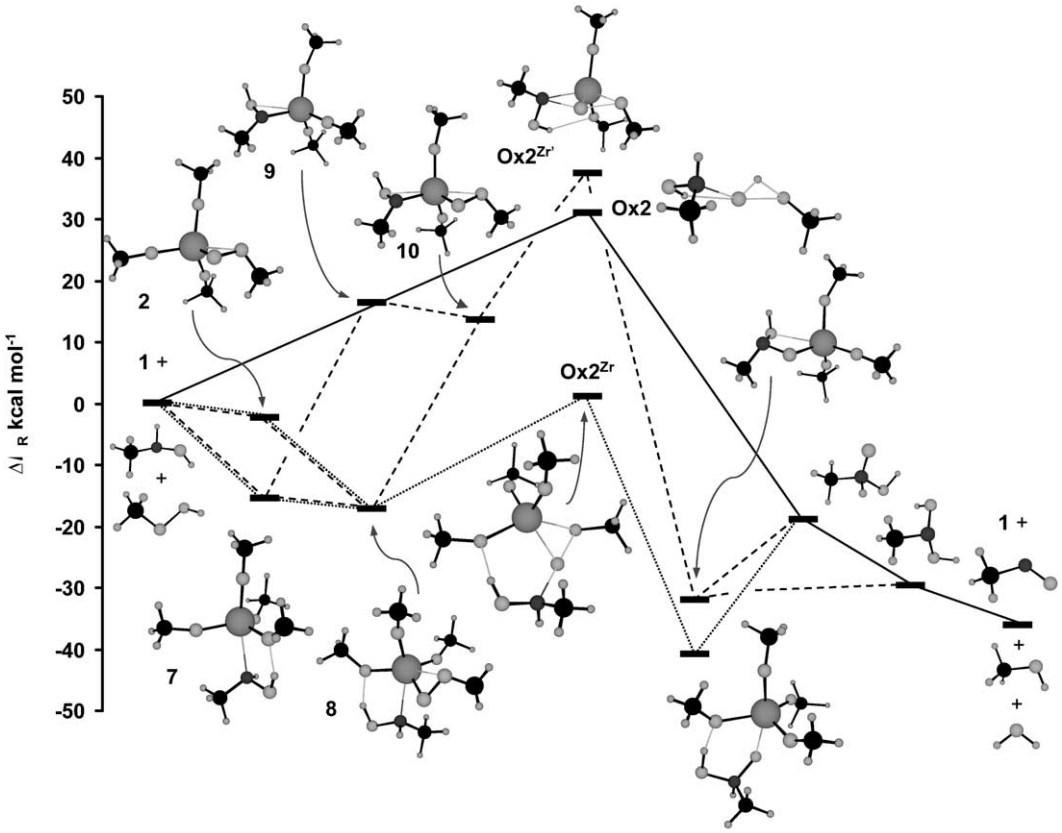


Fig. 3. Calculated pathways for the oxidation of MeNH(OH) to MeNO; —, uncatalyzed reaction; . . . , catalyzed reaction without zirconium amide intermediate; ---, catalyzed reaction with zirconium amide intermediate.

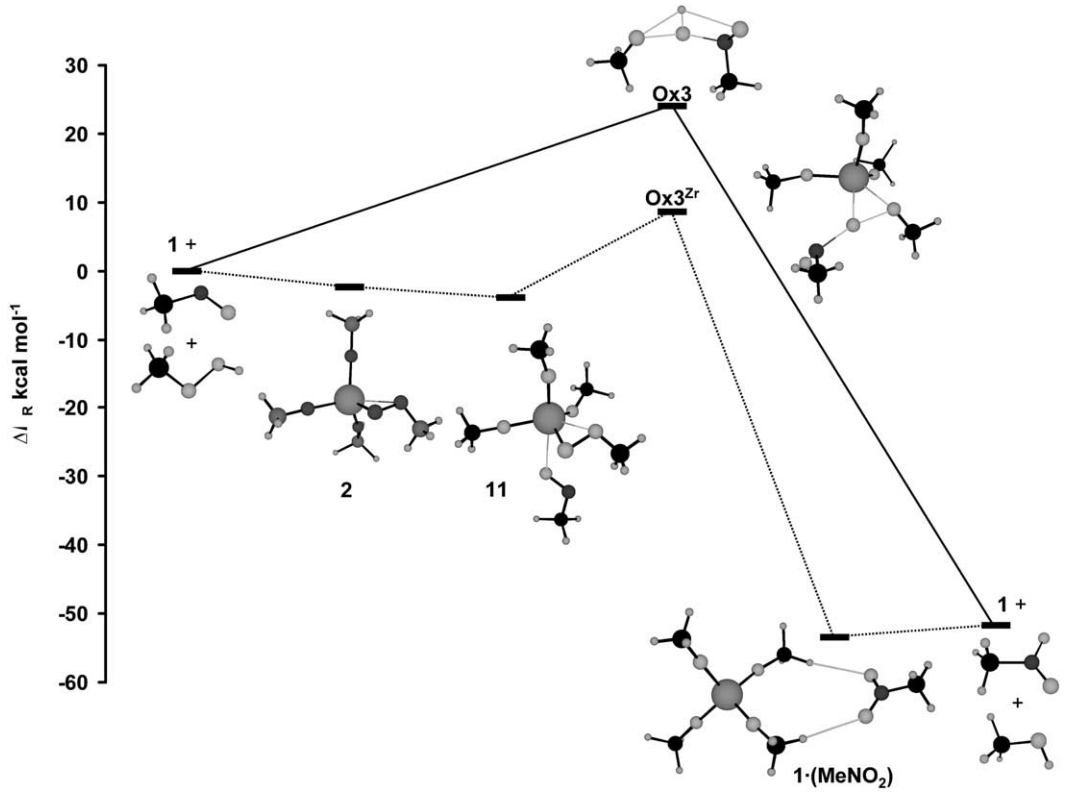


Fig. 4. Calculated pathways for the oxidation of MeNO to $MeNO_2$; —, uncatalyzed reaction; . . . , catalyzed reaction.

geometry of **Ox3**. As expected, the nitrogen atom is found in a trigonal pyramidal environment indicating an nucleophilic attack at the LUMO of MeNO. The OH proton of MeOOH in **Ox3** is not just bridging the O–O unit (as in **Ox1** and **Ox2**) but is found bridging the O–O fragment as well as forming a weak hydrogen bridge to the oxygen atom of the MeNO moiety.

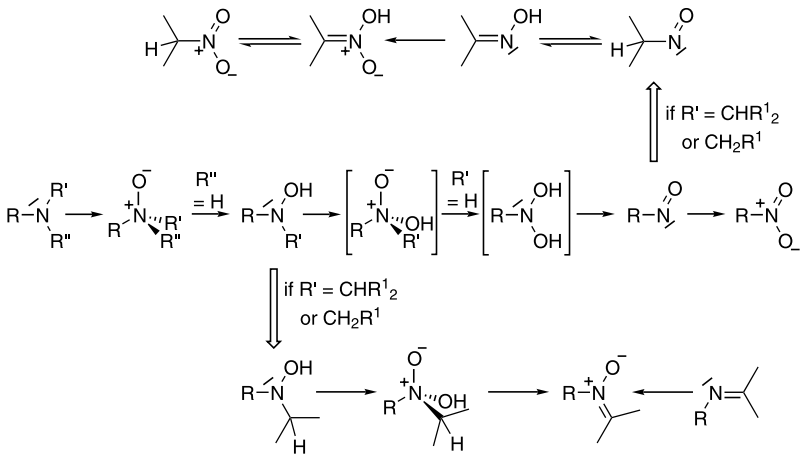
The transition state of the zirconium catalyzed reaction **Ox3^{Zr}** is reached via a week precoordination of MeNO to $Zr(OMe)_3(OOMe)$ (**11**; ΔH_R: −3.9 kcal mol^{-1}). An activation barrier ($\Delta H^{\#}$) of + 8.6 kcal mol^{-1} was calculated for the oxygen transfer. This low barrier agrees with the observation that nitroso derivatives are rapidly oxidized to the corresponding nitro compounds and that the isolation of nitroso compounds from catalytic amine oxidations requires special conditions [49]. The final product CH_3NO_2 is an even poorer donor than CH_3NO. It therefore was not possible to find a stable adduct to the zirconium center. In contrast CH_3NO_2 forms week hydrogen bonds to OMe ligands of $Zr(OMe)_4$ (**1 MeNO$_2$**; ΔH_R: −1.4 kcal mol^{-1}), which are obviously not stable in solution.

These observation are in our opinion of relevance for all *N*-oxidations carried out with oxenoids-like transition metal activated peroxides, dioxiranes or percarboxylic acids—which undergo non-radical type oxygen transfer reactions. Transfer of an oxygen atom to a nitrogen atom will generate an *N*-oxide, which then has alternative pathways for further reactions depending on the substitution patterns of the nitrogen atom and the joint carbon atoms. Subsequent tautomerizations, elimination of water and further oxidation makes nitrogen compounds with special chemical structures and reactivity accessible (Scheme 10).

A special reaction pathway is followed during the oxidation of primary benzylic and allylic amines: oximes are the main product here. They can be hydrolyzed giving an aldehyde and hydroxylamine. Catalysts which are able to oxidize other primary amines can be applied for this reaction. During the last years a series of heterogeneous catalysts have been tested for this reaction, including silicalites like TS-1 [30b,61]. However, molybdenum peroxo complexes and methyltrioxo rhenium(VII) have turned out to be able to catalyze this reaction under homogeneous conditions with H_2O_2 as the oxidizing agent [35,62].

6. Azo and azoxy compounds

Azo compounds can either be generated from azoxy compounds by reduction or by electrophilic aromatic substitution using diazonium cations as coupling reagents. A recently published alternative for the synthesis of symmetrical aromatic azo compounds starting from anilines introduces manganese(III)tetraphenylporphyrin as the catalyst in combination with tetrabutylammonium or sodium periodate. The



Scheme 10.

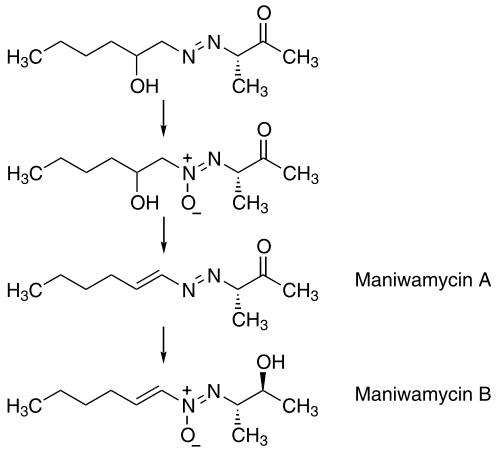
presence of heterocyclic nitrogen bases like imidazole seems to modulate the reactivity of the catalyst by coordination to one of the axial positions [63].

Azoxy compounds can also be obtained by the reduction of nitro compounds, but are synthesized favorably by oxidation of the corresponding, easily available azo derivatives. The application of hydrogen peroxide for the latter reaction was already described about 100 years ago [64]. The desired products are generally obtained in high yields, since the oxidation of the second nitrogen atom is difficult due to deactivation by the first NO moiety. A whole series of oxidation reagents has been reported to be suitable for this conversion during the years: hydrogen peroxide in acetic acid, percarboxylic acids, perphosphoric acid or $PhI(OAc)_2$ [65]. For two of these systems, the oxidation of sulfanilic acid by peroxomonophosphoric acid and the oxidation of *trans*-azobenzenes with peroxybenzoic acid, detailed mechanistic studies were carried out [66]. These investigations prove a one step transfer of the oxygen atom to nitrogen by the oxenoid reagent, which is correlating with our theoretical study discussed above.

It is therefore not surprising, that there are a multitude of transition metal catalyzed oxidations of azo compounds working under mild conditions and giving high yields of azoxy derivatives. Heterogeneous titanium or vanadium silicalites and zeolithes [67] have turned out to be active catalysts for this reaction as well as series of group VI transition metal complexes, [68] all applied in combination with hydrogen peroxide.

$VO(acac)_2$ which is known to catalyze the epoxidation of allylic alcohols in the presence of ^{t}BuOOH has been introduced into the regioselective *N*-oxidation of β-hydroxy azo compounds, [69] which opened up a new synthesis of the antifungal antibiotic Maniwamycin A and the related Maniwamycin B (Scheme 11).

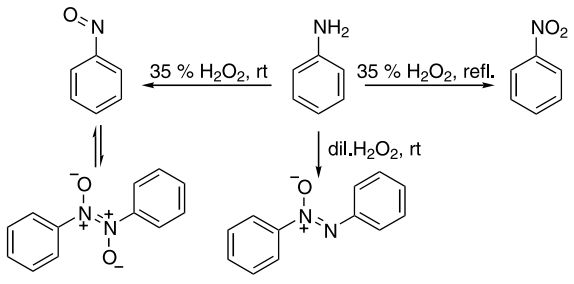
The *N*-oxidation of the azo compound is performed with high regioselectivity, probably due to a coordination of the substrate to the vanadium catalyst, as it is known from the formation of allylic epoxides.



Scheme 11.

An interesting example for the influence of the reaction conditions on the distribution of the products of *N*-oxidations in general is shown on Scheme 12.

The oxidation of aromatic amines with hydrogen peroxide catalyzed by the cetylpyridinium heteroperoxotungstate $[C_5H_5N\text{-}(CH_2)_{15}CH_3]_3\{PO_4[WO(O_2)_2]_4\}$ was investigated by Ishii and coworkers [70]. The starting materials are selectively converted to nitroso compounds, which are in equilibrium with their dimers at room temperature in a two-phase mixture of chloroform and 35% H_2O_2. Carrying out the



Scheme 12.

same reaction under reflux conditions leads to nitro derivatives, while the oxidation of aniline in diluted H_2O_2 produces azoxybenzene with high selectivity.

7. Conclusion

Covering all special aspects of *N*-oxidation could not be the intention of this review. This is almost impossible due to the widespread fields of research opened up here. For example, oxidative dehydrogenation of amines to imines, one of the central processes in the biochemistry of amino acids, could not be included. The role of transition metals in such reactions was recently summarized in an excellent review article [71]. We therefore focussed on two central points of this kind of chemistry: the synthetic benefit and the interesting mechanisms of these multistep oxidations. The detailed discussion of novel mechanistic insights should be helpful in systematizing and understanding each single oxygen transfer process as a consequence of the substitution pattern at nitrogen.

Further Reading

See ref.[61].

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