EFFECTIVE CATALYTIC OXIDATION OF 1-ALKENES USING PALLADIUM-NITRO COMPLEXES IN THE PRESENCE OF AMIDES.

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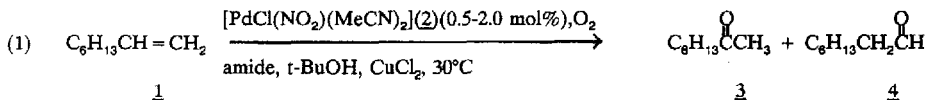Koninklijke/Shell Laboratorium Amsterdam (Shell Research B.V.), P.O. Box 1003 AA Amsterdam, The Netherlands

Abstract. The rate of oxidation and the catalyst stability in the oxidation of 1-alkenes with O_2 using $[PdCl(NO_2)(MeCN)_2]$ as catalyst is considerably improved by the use of amides as ligands or solvents.

Transition metal catalyzed oxidation of olefins with molecular oxygen has attracted considerable attention from a synthetic, mechanistic, and industrial point of view[1]. Environmental constraints with commonly used oxidants and the formation of stoichiometric amounts of co-products are important incentives to develop selective nonradical oxidations with O_2. Various transition-metal dioxygen complexes and studies of oxygen activation have recently been described.[2,3].
The Wacker process, based on palladium dichloride is extremely useful for the conversion of vinyl-substituted compounds into methylketones although there are severe limitations for higher α-olefins due to olefin isomerization or low catalyst stability[1,4]. It has been demonstrated that catalysts based on palladium (II) nitro complexes in some cases offer an excellent alternative to the Wacker oxidation[5]. We reported that $[PdCl(NO_2)(MeCN)_2]$, modified with $CuCl_2$ as co-catalyst and t-BuOH or i-PrOH as ligand or solvent, is capable of catalyzing the oxidation of α-olefins to aldehydes (60-70% selectivity) or methylketones (>90% selectivity) using molecular oxygen[6]. The proposed catalytic cycle for the oxidation of 1-alkenes to aldehydes, which involves a palladium-nitro-nitrosyl redox couple,[7,8] is shown in scheme I.
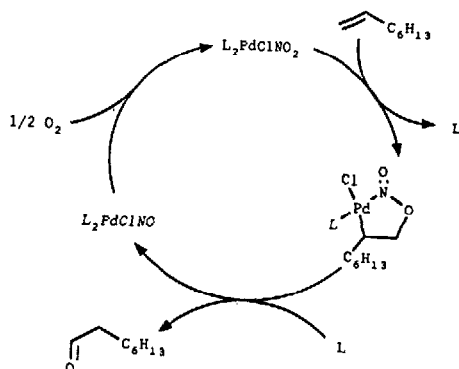
Scheme I. Catalytic cycle for the oxidation of 1-alkenes to aldehydes with O_2 using a [Pd-NO$_2$] catalyst.

In this paper a remarkable improvement is described in the catalytic oxidation of α-olefins with [PdCl(NO$_2$)(MeCN)$_2$], CuCl$_2$ and O$_2$ (eq.1), when amides are used as ligands or solvents.

$$(1) \quad C_6H_{13}CH=CH_2 \xrightarrow[\text{amide, } t\text{-BuOH, CuCl}_2, 30°C]{[PdCl(NO_2)(MeCN)_2](\underline{2})(0.5\text{-}2.0 \text{ mol\%}),O_2} C_6H_{13}\overset{O}{\overset{\|}{C}}CH_3 + C_6H_{13}CH_2\overset{O}{\overset{\|}{C}}H$$

$$\underline{1} \hspace{8cm} \underline{3} \hspace{2cm} \underline{4}$$

The oxidation of 1-octene with O$_2$ to 2-octanone ($\underline{3}$) or octanal ($\underline{4}$) was studied as a model reaction. In a typical procedure, the catalyst was prepared in situ from [PdCl(NO$_2$)(MeCN)$_2$](2 mol%), CuCl$_2$ (8 mol %) in t-BuOH or t-BuOH/amide solvent mixtures at 50°C, and the oxidation of $\underline{1}$ was subsequently performed at 30°C under 1 atm. of O$_2$[9]. The results of the variation of alcohol, amide and CuCl$_2$ on the oxidation of $\underline{1}$ are summarized in table I.

Table I . Oxidation of 1-octene mediated by [PdCl(NO$_2$)(MeCN)$_2$]($\underline{2}$)

entry	catalyst[a]	reaction time (h)	octanal[b]	2-octanone[b]	octene isomers
1	$\underline{2}$,CuCl$_2$,tBuOH	4	5.0	1.7	0.1
2	$\underline{2}$,CuCl$_2$,iPrOH	16	0.3	5.0	1.3
3	$\underline{2}$,CuCl$_2$,tBuOH/ 10eq.DPA[c]	2	5.1	3.1	0.5
4	$\underline{2}$,CuCl$_2$,tBuOH/ DPA,2:1	4	7.8	29.9	4.0
5	$\underline{2}$,CuCl$_2$,tBuOH/ DPA,1:1	4	3.8	40.1	2.0
6	PdCl$_2$,CuCl$_2$ DPA/H$_2$O,9:1	4	0.5	13.7	33.0
7	$\underline{2}$,tBuOH/ DPA,1:1	0.6	-	4.0	14.0
8	$\underline{2}$,CuCl$_2$,[d] tBuOH/DPA,2:1	20	14.5	47.7	15.9

a) See text; [PdCl(NO$_2$)(MeCN)$_2$] (2 mol%), CuCl$_2$ (8 mol%), 30°C. b) Yields (bij GC) in equivalents based on Pd. c) DPA = N,N-diethylpivaloylamide ($\underline{5}$); 1.0 mol% of $\underline{2}$. d) [PdCl(NO$_2$)(MeCN)$_2$] (1 mol%).

In contrast to the oxidation in acetonitriles or under Wacker conditions (entry 6)[5] the use of alcohols as the solvent leads to almost complete inhibition of octene isomerization. Furthermore the use of t-BuOH instead of i-PrOH as the solvent mainly results in a change of the regioselectivity (entries 1,2). An as yet unprecedented[7] high selectivity ($\geq 75\%$) towards aldehyde formation in the oxidation of an α-olefin with O$_2$ is found. From entries 1-3 it is clear that small amounts of N,N-diethylpivaloylamide ($\underline{5}$) hardly effect aldehyde formation (approximately twofold rate increase) but increasing amounts of $\underline{5}$ (entries 4,5) result in a strong enhancement of the rate of ketone formation. The use of PdCl$_2$ instead of [PdCl(NO$_2$)(MeCN)$_2$] results in a typical Wacker process (entry 6); omission of H$_2$O did not give any oxidation. From entry 7 it is also clear that CuCl$_2$ is essential for a high turnover number, although the system is still catalytically active without CuCl$_2$.

It should be noticed that the isomerization of 1-octene is strongly suppressed, and in most cases negligible, in the present catalytic system in contrast to the oxidation without CuCl$_2$ (entry 7) or oxidations under Wacker conditions (entry 6). In the latter case octene isomers are the major products. The formation of only small amounts of isomeric alkenes is a prime feature of this new oxidation. As well as the rate of oxidation the stability of the oxidation catalyst is improved when amide $\underline{5}$ is used (entry 8), resulting in a turnover of 62 (20 h). The amount of isomeric alkenes increases after prolonged reaction times.

Thus so far only palladium-nitro complexes containing nitrile ligands have been used[5,8,10]. After the discovery that the presence of 5 has a beneficial effect on these catalytic oxidations, a study of amide modification was undertaken (table II). The results in table II show that the "rate-enhancing effect" with amide 5 as the co-solvent occurs both in t-BuOH and i-PrOH, alkene isomerization being faster in i-PrOH (entries 1,2). It is remarkable that especially amides derived from bulky

Table II. Effects of amides on the 1-octene oxidation[a]

entry	Amide	(%)[b,c]	octanal[d]	2-octanone[d]	octene[d] isomers	remarks
1	5	50	2.0	25.4	3.2	0.5% cat.
2	5	40	3.2	31.0	12.0	0.5% cat. co-solvent i-PrOH
3	6	10	0.1	0.1	0.2	
4	7	7	3.6	3.9	1.0	
5	8	100	-	-	-	
6	9	30 eq.	0.3	1.9	1.2	
7	10	20	0.5	3.3	1.0	18 h
8	11	20	2.4	11.5	5.0	18 h
9	12	20	3.7	4.7	7.0	18 h
10	13	15	-	-	-	
11	14	7 eq.	6.5	4.4	0.9	3 h
12	14	100	0.5	13.1	14.3	
13	15		6.5	3.3	1.0	PdClNO$_2$2DMA (17)
14	16		1.5	4.6	4.0	PdClNO$_x$2DMF (18), 18 h
15	15		9.9	9.3	9.9	PdClNO$_2$2DMA + CuCl$_2$ 2DMA, 18 h

a) [PdCl(NO$_2$)(MeCN)$_2$] (2 mol%) / CuCl$_2$ (8 mol%) / O$_2$ (1 atm.) / 30°C. b) The solvent is a mixture of t-BuOH and an amide (w.t. %). c) 5 Me$_3$CCONEt$_2$, 6 MeCONHCMe$_3$, 7 Cl$_3$CCONHCMe$_3$, 8 N-Methylpyrrolidone, 9 Me$_3$CCON(allyl)$_2$, 10 C$_6$H$_5$CONEt$_2$, 11 p-MeOC$_6$H$_4$CONEt$_2$, 12 p-O$_2$NC$_6$H$_4$CONEt$_2$, 13 HO$_2$CCH$_2$CH$_2$CONEt$_2$, 14 Et$_2$NCOCONEt$_2$, 15 Me$_2$NCOCH$_3$, 16 Me$_2$NCOH. d) The amount of product is given after 4 h. in equivalents based on Pd.
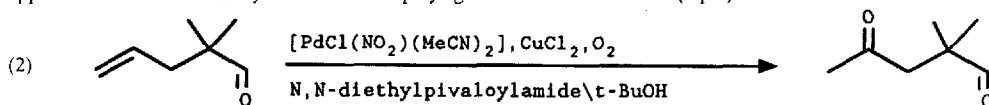
carboxylic acids give higher rates as solvent or co-solvent in the oxidation of 1-octene to 2-octanone (entries 1,4,6). Aromatic amides (entries 7-9) increase the oxidation rate but simultaneously increase the rate of isomerization. An additional carboxylic acid functionality in the ligand (entry 10) deactivates the catalyst. The use of stoichiometric amounts of N,N-dimethylformamide decreases the reactivity and also gives more ketone than aldehyde. The use of stoichiometric amounts of N,N-dimethylacetamide (DMA) does not have a large effect on the catalytic system. Similar results are observed with complexes 17 and 18 (entries 13-15). In contrast to the promoting effects of amides in the Wacker oxidation[10], larger amounts of DMF or DMA result in complete deactivation of the present catalyst. This effect was also found for other strongly coordinating ligands such as acetonitrile.

Oxalic acid amide 14 is very well suited as ligand or solvent for the oxidation of 1-octene (entries 11,12). An active binuclear palladium-nitro complex is formed upon reaction of [PdCl(NO$_2$)(MeCN)$_2$] and N,N'-tetraethyloxalic acid amide 14[11] and even with a large excess of amide only one molecule of ligand 14 is bound to two Pd-atoms.

This is probably the reason why oxalic amides can be used in large excess during the oxidation reactions without deactivating the catalyst. Attempts to prepare complexes of [PdCl(NO$_2$)(MeCN)$_2$] and bulky amides have so far resulted in the isolation of starting materials, presumably due to weak coordination. These bulky amides can be used, however, very well as solvent or co-solvent in the oxidation of 1-octene to 2-octanone with improved activity and stability of the catalyst. Less bulky amides probably block the necessary coordination sites for the olefin and as a consequence low activity towards oxidation is observed[12].

Finally the selective conversion of 2,2-dimethyl-4-penten-1-al (19) to 2,2-dimethyl-4-oxo-pentanal (20) illustrates a synthetic

application of this new catalytic oxidation employing a functionalized alkene (eq. 2).

(2)

$$\text{[PdCl(NO}_2\text{)(MeCN)}_2\text{], CuCl}_2\text{, O}_2 \xrightarrow{\hspace{2cm}} \text{N,N-diethylpivaloylamide\textbackslash t-BuOH}$$

A quantitative oxidation of 19 to 20 (1.4 g scale) was found using O_2 and 0.4 mol% of catalyst, prepared in situ from [PdCl(NO$_2$)(MeCN)$_2$] and CuCl$_2$. A reaction time of 8 h was sufficient instead of 60 h reported for a similar oxidation with PdCl$_2$ under Wacker conditions[13]. It can be concluded that the use of bulky amides as (co-)solvents for the [PdCl(NO$_2$)(MeCN)$_2$] catalyzed oxidation of alkenes with O_2 offers an useful alternative to Wacker type oxidations. Mechanistic investigations to elucidate the origin of the "amide effect" are in progress.

References and Notes

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9.   All compounds showed ^{1}H NMR, ^{13}C NMR, IR and HRMS data in accordance with their structures, or where identical with independently prepared samples. For the catalyst preparation, see ref. 7. Isooctane was used as an internal standard for the GC analyses. All ligands were prepared by standard methodology.

10.   The Wacker oxidation has been improved considerably by the use of DMF as a co-solvent although turnover numbers are still rather low; Tsuji, J.; Nagashima, H.; Nemoto, H. Org. Synth. 1984, 62, 9.

11.   The binuclear palladium complex Pd$_2$C$_{10}$H$_{24}$N$_4$O$_6$Cl$_2$(C,H,N,Pd analysis) was isolated and proved to be active in the catalytic oxidation of 1-octene. Unfortunately an X-ray structural analysis was not successful sofar.

12.   The preliminary results shown in Table II indicate that with amide ligands a delicate balance exists between catalyst activation and deactivation.

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