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CATALYTIC OXIDATION OF 1-ALKENES WITH MOLECULAR OXYGEN AND PALLADIUM NITRO COMPLEXES

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SUMMARY

(CH₃CN)₂PdClNO₂ is capable of catalysing the oxidation of 1-alkenes to methyl ketones, epoxides (refs. 1-9) and aldehydes (ref. 6) using molecular oxygen. In this paper we report the influence of solvent, co-catalyst and additional ligands on the reactivity and selectivity in the oxidation of 1-alkenes to aldehydes by (CH₃CN)₂PdClNO₂.

INTRODUCTION

Selective catalytic oxidations of alkenes with molecular oxygen are commercially important and synthetically useful processes (ref. 10). It is well-known that 1-alkenes can be selectively oxidized to methyl ketones (ref. 11). Based on this oxidation reaction alkenes can be regarded as masked ketones.

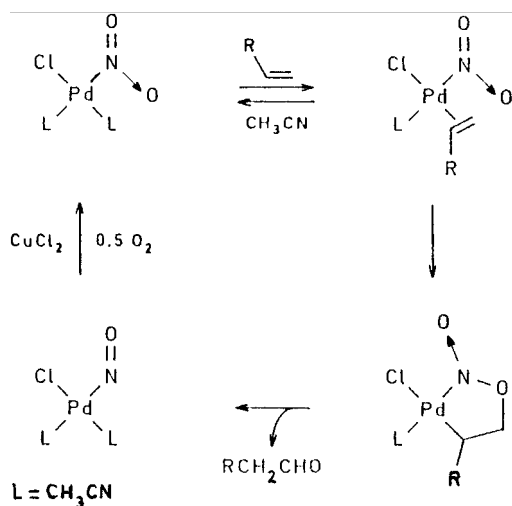
Oxidation reactions of alkenes with molecular oxygen mediated by (CH₃CN)₂PdClNO₂ have been described (refs. 1-9). Alkenes are generally oxidized to the corresponding ketones (refs. 1,2,4,6,7). With specific alkenes epoxides were formed (refs. 3,4,7,8,9). However, we observed aldehyde formation in a good yield using (CH₃CN)₂PdClNO₂ as catalyst with t-butyl alcohol as solvent and CuCl₂ as co-catalyst (ref. 6). It is assumed that the oxidation of alkenes to ketones goes by an intramolecular nucleophilic attack of the nitro group on the palladium bonded alkene followed by a hydride shift (refs. 1-9,12,13). We assume that formation of aldehydes goes by a comparable mechanism (scheme 1).

We now report the influence of solvent, co-catalyst and additional ligands on the catalytic oxidation reaction.

RESULTS AND DISCUSSION

In a typical oxidation reaction 1-octene was converted using a catalyst (5 mol %) prepared from (CH₃CN)₂PdClNO₂, CuCl₂ in an oxygen-saturated solution of t-butyl alcohol. After a reaction time of 16 hours under an oxygen atmosphere octanal and 2-octanone (ratio 60:40) were obtained in a 970 % combined yield based on (CH₃CN)₂PdClNO₂. A low isomerization activity was observed resulting in

the formation of 80 % (based on Pd) octene isomers. The proposed mechanism for the catalytic oxidation of 1-alkenes to aldehydes is given in scheme 1.



Scheme 1. The proposed mechanism for the catalytic oxidation of 1-alkenes to aldehydes by molecular oxygen mediated by $(\text{CH}_3\text{CN})_2\text{PdClNO}_2$.

We propose that the regioselectivity in the cycloaddition of the alkene coordinated to the palladium nitro catalyst, determines the aldehyde to ketone ratio. It may be anticipated that the constitution of the palladium nitro complex and the nature of the ligands strongly influence the stereoselectivity in the cyclisation step. Subtle effects on the stereochemical results of 1,3-dipolar cycloaddition to alkenes are well precedented and the mechanistic pathways described above certainly show similarities with 1,3-dipolar cycloaddition reactions (ref. 14).

Preliminary experiments showed that several factors like metal salts, solvent and ligands influence the reactivity and selectivity of the oxidation reaction. In order to assess these factors we have undertaken a systematic investigation. The results on variation in solvent, co-catalyst and ligands are described here-with.

The influence of solvent on the oxidation reaction is summarized in table 1. Entry 2,3,4 and 7 show the strong tendency of Pd(II) complexes to catalyse the selective oxidation of 1-alkenes to methyl ketones. Coordinating solvents almost completely inhibits the oxidation reaction and results in isomerization of the starting 1-alkene. Possibly this effect is due to blocking of the necessary coordination places at palladium or is the result of a fast substitution of the

coordinated alkene.

TABLE 1

Oxidation of 1-octene. 0.2 mmol $(\text{CH}_3\text{CN})_2\text{PdClNO}_2$ + 0.8 mmol CuCl_2 + 4 mmol 1-octene, 25 ml solvent, 50°C. (Product determination (GC) after 16 hours, amounts in % based on Pd).

Entry	Solvent	Octanal	2-Octanone	Octene isomers
1	t-butyl alcohol	580	390	80
2*	t-amyl alcohol	170	1490	460
3	isopropyl alcohol	<30	500	130
4	hydroxyacetone	<30	1000	<30
5	2-hydroxypropionitrile	-	-	-
6	acetonitrile	-	-	-
7	toluene	<30	300	100
8	nitromethane	40	30	50
9	acetone	-	<30	500
10	HMPA	-	<30	500
11	DMF	<30	<30	<100

*Reaction time of 8 hours.

In apolar solvents we only observed a very slow reaction, partially due to the low solubility of the catalyst in these solvents. So far t-butyl alcohol is the only solvent in which aldehyde than ketone can be obtained.

The role of CuCl_2 , the co-catalyst, in the classical Wacker oxidation is to oxidize Pd(0) to Pd(II). The effect of co-catalyst on the oxidation of 1-octene with $(\text{CH}_3\text{CN})_2\text{PdClNO}_2$ in t-butyl alcohol is summarized in table 2.

TABLE 2

The influence of co-catalyst on the oxidation of 1-alkene. Reaction in t-butyl alcohol, at 30°C with 20 equivalents (based on Pd) of 1-octene. The amount of co-catalyst and of products (GC) are based on Pd.

Entry	Co-catalyst (eq)	Reaction time (h)	Octanal (eq)	2-Octanone (eq)	Octene isomers (eq)
1*	4 CuCl_2	16	6	4	1
12	4 CuCl_2	4	6	3	1
13	1 CuCl_2	19	1	4	9
14	10 CuCl_2	5	2	0.5	1
15	15 CuCl_2	5	2	0.5	1
16	4 CuCl_2	0.5	-	1	19
17	4 CuCN	2	0.2	0.7	10

TABLE 2 (continued)

Entry	Co-catalyst (eq)	Reaction time (h)	Octanal (eq)	2-Octanone (eq)	Octene isomers (eq)
18**	4 Cu(ClO ₄) ₂ ·6H ₂ O	1	5	19	56
19	4 Cu(CO ₃)Cu(OH) ₂	2	-	-	8
20	4 CuCl ₂ + 1 LiCl	7	5	6	2
21	4 CuCl ₂ + 1 LiF	4	4	3	6
22	2 CuCl ₂ + 2 SnCl ₂	0.5	1	3	15
23	2 CuCl ₂ + 2 CoCl ₂	1	-	-	15
24	2 CuCl ₂ + 2 NiCl ₂	1	-	-	14

*Reaction temperature of 50°C.

**100 Equivalents of 1-octene.

Increasing the amount of CuCl₂ shows a maximum in the reactivity and the selectivity to aldehyde formation using four equivalents of CuCl₂. Decreasing the amount of CuCl₂ gives an increase in isomerization rate and a decrease in oxidation rate and selectivity. Increasing the amount of CuCl₂ beyond four equivalents shows only a small influence on the oxidation reaction, but increases the isomerization rate. Substituting two equivalents of CuCl₂ for other metal salts like SnCl₂, FeCl₃, ZnCl₂, NiCl₂, HgCl₂, CoCl₂ or PdCl₂ results in the acceleration of isomerization reaction and gives only small amounts of ketones and aldehydes. The enhanced isomerization using other metal halides than CuCl₂ might be attributed to a Lewis acid effect on the palladium catalysed reactions.

The role of CuCl₂ in the Wacker oxidation is well established. The role of CuCl₂ in the oxidation of 1-alkenes by (CH₃CN)₂PdClNO₂ is however not completely clear. In table 2 it is shown that not only the oxidation rate but also the selectivity of the oxidation reaction strongly depends on the amount of CuCl₂ used. We therefore assume that the active species in the formation of aldehydes is not just a palladium nitro complex, but a species that also contains CuCl₂, presumably a chloride bridged binuclear complex. Unfortunately we were not yet able to isolate such a species to prove our assumption.

In table 1 it is shown that the oxidation reaction was almost completely inhibited using coordinating solvents (entry 5,6,10,11). The effects of additional ligands on the oxidation reaction of 1-octene by (CH₃CN)₂PdClNO₂-4CuCl₂ in *t*-butyl alcohol under an oxygen atmosphere is summarized in table 3. It was shown (ref. 12) that NO₂⁻ easily dissociates from palladium. However, we found that increasing the amount of NO₂⁻ in solution by adding KNO₂ (entry 26,27) leads to an increase in the isomerization rate and in a decrease of the oxidation reaction rate. This effect was even much stronger using an NO₂ atmosphere above the

reaction medium.

TABLE 3

Ligand effect on the oxidation of 1-octene. Reaction of $(\text{CH}_3\text{CN})_2\text{PdClNO}_2\text{-4CuCl}_2$ in t-butyl alcohol at 50°C with 20 equivalents (based on Pd) of 1-octene, amount of ligand and product (GC) based on Pd.

Entry	ligand	Amount (eq)	Reaction time (h)	Octanal (%)	2-Octa- none (%)	Octene isom.(%)
12	-	-	4	600	300	100
25	NO_2 (atmosphere)		5	<20	180	1350
26	KNO_2	2	4	125	125	375
27	KNO_2	4	4	50	50	300
28	acetonitrile	4	8	200	250	850
29	2-hydroxypropionitrile	2	3	80	50	<10
30	trichloroacetonitrile	2	0.1	<50	<50	>500
31	HMPA	2	3	<50	<50	700
32	$(\text{CH}_3\text{CN})_2\text{PdBrNO}_2$	-	19	390	690	540

Addition of nitriles increases the isomerization rate and decreases the oxidation rate, probably by blocking the necessary coordination places on palladium or by a fast substitution of the coordinated alkene by the added ligands.

CONCLUSIONS

The reactivity and selectivity of the oxidation reaction of 1-octene to octanal using molecular oxygen and $(\text{CH}_3\text{CN})_2\text{PdClNO}_2$ strongly depends on the reaction conditions. Reasonable amounts of aldehyde are only observed in t-butyl alcohol using four equivalents of CuCl_2 as the co-catalyst. The oxidation of other alkenes is now under investigation and will be reported later.

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H. MIMOUN (Lab. d'Oxydation Inst. Franc. Petrole, France): Did you observe Pd(0) precipitation? How can you explain the antimarkovnikov oxidation induced by t-BuOH? Did you try t-BuO⁻ ligands on Pd?

N.H. KIERS (University of Groningen, The Netherlands): In some cases we observed a small amount of Pd(0) precipitation after about 4 turnovers, resulting in an increase of the isomerisation rate and a decrease in the selectivity towards aldehyde formation. We were not able to make a complex containing both NO₂⁻ and t-BuO⁻ ligands. Oxidation reactions using Cu(O^tBu) or Cu(O^tBu)₂ instead of CuCl₂ were not successful.

G. FRANZ (Fa. Huls AG, BRD): Comment on Wacker Process: Scientists of some institutes of Sibirian Branch of Academie of Sciences of USSR have some years ago succeeded in replacing CuCl₂ by heteropolycacids in the Wacker Process. Therefore Cu is not essential in this system. Pd is a very effective decarbonylation catalyst of aldehydes. Did you ever pay attention to decarbonylation products during your experimental studies?

N.H. KIERS (University of Groningen, The Netherlands): The main difference between the Wacker oxidation and our oxidation process is the use of a Pd(II)-NO₂ / Pd(II)-NO instead of a Pd(II) / Pd(0) couple. In our system Pd(II) is not reduced. We followed the oxidation reactions with GC/MS and we did not observe the formation of decarbonylation products.

J.M. BRÉGEAULT (Univ. P et M. Curie, France): Did you observe the formation of chlorinated products when you work with an excess of CuCl₂? What about the decay period of your system?

N.H. KIERS (University of Groningen, The Netherlands): We did not observe chlorinated products. The decay period strongly depends upon the conditions under which the catalytic system is prepared. Without pre-preparation we observed a slow reaction and a decay of the reaction after about 4 hours. With pre-preparation of the catalyst by stirring the mixture of (CH₃CN)₂PdClNO₂ and CuCl₂ under an oxygen atmosphere for about 5 hours we observed a fast oxidation reaction but also a rapid decay of the reaction after about 20 minutes.

G. STRUKUL (Dip. di Chimica Univ. Venezia, Italy): The formation of aldehydes in your system requires oxygen transfer at the C₁ instead of C₂ as normally happens. Also, it is clear that this unusual behavior depends on t-BuOH and the Cu co-catalyst. Do you have any suggestions for this unusual behavior?

N.H. KIERS (University of Groningen, The Netherlands): What we propose as the catalyst is a dinuclear complex, containing both Pd and Cu in which t-BuOH is acting as a bridging ligand. Steric effects are probably the main reasons for the coordination of the alkene in such a way that oxygen transfer to C₁ becomes more facile.

A.J. CHALK (Givaudan Corp., U.S.A.): Is it possible that terminal epoxides are intermediates in this reaction and that they rearrange to the mixture of ketone and aldehyde? Have you tried adding terminal epoxides to the reaction mixture to see if they isomerise to test this possibility?

N.H. KIERS (University of Groningen, The Netherlands): Epoxides do react under the reaction conditions used, but they give a mixture of t-butyl ethers which are not observed in the oxidation reaction of 1-alkenes. We did not observe the corresponding aldehydes or ketones in the reaction with terminal epoxides.

B.R. JAMES (Dept. of Chem. Univ. of British Columbia, Canada): You state that "the role of CuCl_2 in the Wacker oxidation is well established". I am not convinced that this is so. I believe that mixed, metal species ($\text{Pd}_2\text{Cu}?$), but ill-characterised, have been isolated from Wacker systems. In your system you imply that CuCl_2 is a ligand, and so this part of the catalytic cycle may not be so different to that in the Wacker cycle. It would be of value to continue the attempt to isolate such bimetallic species.

N.H. KIERS (University of Groningen, The Netherlands): The Wacker oxidation process does not work without a co-catalyst like CuCl_2 to oxidize Pd(0) to Pd(II). However, CuCl_2 is not essential for the reoxidation of Pd-NO to Pd- NO_2 , but has an enormous influence on the selectivity of the oxidation reaction. This implies a different role for CuCl_2 in our system. We will continue our efforts to isolate a (bimetallic) complex which is active in the oxidation of 1-alkanes to aldehydes.