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REGIOSELECTIVE HYDRATION OF ACRYLONITRILE TO GIVE ACRYLAMIDE CATALYZED BY $[Pd(OH)_2(bipyridine)(H_2O)]$

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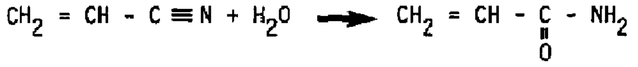
ABSTRACT : Satisfactory yields were observed for the selective hydration of acrylonitrile to give acrylamide when using the complex $[Pd(OH)_2(bipy)(H_2O)]$

Since acrylamide is a very useful synthetic intermediate and is largely used in the traitment of waste water as floculant agent or in the assisted recovery of petroleum, several procedures to obtain it were previously proposed especially by hydration of acrylonitrile (1).



$$CH_2 = CH - C \equiv N + H_2O \longrightarrow CH_2 = CH - \underset{\underset{O}{\|}}{C} - NH_2$$

However the preparation of the catalysts for this reaction are often tedious and expensive (1a, 1b, 1c). Although there are high yields the catalyst/acrylonitrile ratios are frequently > 1 (1d, 1e). Moreover the reaction needs high temperatures (1f) and sometimes high pressures (1f). Whereas the anchorage of the catalysts on various insoluble supports allowed some authors to simplified procedures, the yields remained low and the selectivity was thus decreased (1g, 1h).

This communication deals with the homogeneous catalysis by palladium complexes which allow soft experimental conditions of temperature (50-70°C) and pressure (1 atm.) as well as the regioselectivity since the hydration of the carbon double bond is to be avoid. Using the complex $[PdCl(OH)(bipy)(H_2O)]^{\dagger}$ (1), previously studied for the hydration of acetonitrile (2), we observed 13 % of conversion for 4 h. However the concentration in acrylonitrile was low, i.e. 1.4 mol l^{-1}. By changing the nature of the ligand we did not observe

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† abbreviations 2,2'-bipyridine, bipy ; ortho-phenantroline, o-phen ; tetramethyl ethylenediamine TMEDA ; diphenylphosphino ethane, DPPE

significant variations in the yields except for the TMEDA ligand : [PdCl(OH)(o-phen)(H_2O)] (2) 13 %, [PdCl(OH)(DPPE)(H_2O)] (3) 10 %, [PdCl(OH)(TMEDA)(H_2O)] (4) 4 %. However by metathesis of the Cl^- anion in the first complex we prepared the complexes [PdBr(OH)(bipy)(H_2O)] (5), [Pd(CH_3COO)(OH)(bipy)(H_2O)] (6), [Pd$(OH)_2$(bipy)(H_2O)] (7) which gave rise to 13, 11 and 22 % yields respectively. Except for 7, a slight decomposition was observed. But in any case the acrylonitrile was selectively transformed in acrylamide. The complexes 2 - 6 were prepared according to the procedure used for 1 (2). Starting from 0.7 g (2.1 mmol) of $PdCl_2$(bipy) we prepared 7 by heating at 75°C for 6 h in 300 ml of water with a slight excess of a weak anionic exchange resin (20 g, 9.5 meq OH^-). Filtration off of the resin and evaporation of water under reduced pressure gave 0.63 g of 7 in a *pure form* : *yield* 95 %, elemental analysis calculated % for $C_{10}H_{12}N_2O_3Pd$ (found %) : C 38.16 (37.09), H 3.82 (4.02), N 8.90 (8.65), Pd 33.83 (32.89). Moreover addition of the stoichiometric quantity of an acid HX allowed us to recover the complexes 1 - 7 from the solution by precipitation of PdX_2(bipy). After recovery of this insoluble material by filtration, distillation of acrylonitrile and water under reduced pressure gave acrylamide in a pure form.

It should be noted that, at 70°, 7 gave traces of decomposition together with traces of polymerization of acrylonitrile. For this reason we performed our studies at 60° for which lower yields were observed (for instance 20 % for 4 h instead 28 % at 70°) in absence of any decomposition.

In homogeneous phase, i.e. in the presence of few quantities of acrylonitrile, the increase of the concentration of 7 increases the initial rate of hydration e.g. 10 %, 18 % and 21 % for 1 h when the concentrations are 5, 10 and 15 mmol l^{-1} respectively. However it was not possible to exceed 32 % for 10 h in each case.

Thus, in order to obtain higher yields, we tried to perform the hydration in the presence of larger quantities of nitrile and therefore having in the hands two phases. By variation of the volume of acrylonitrile to the volume of water ratio we determined the turn-over reported in table 1.

Table 1 - Turn-over number obtained by variation of the acrylonitrile/water ratio in 1 hour

ratio	3/15	5/25	16/25	1	50/5
turn-over number	30	30	28	33	7

The reaction remained selective in acrylamide ; when the quantities of water decreased the yield decreased significantly and simultaneously some decomposition of the complex appeared.

Keeping a 1/1 ratio for the reactants we examined the effects of various concentrations for the catalyst 7. Table II shows the turn-over numbers calculated after four reactions times.

Table II - Effect of the concentration of the catalyst, using a 1/1 acrylonitrile/water ratio

catalyst	Turn-over number			
	1 h	2 h	3 h	5 h
1.5 10^{-4} mol.	37	57	67	80
3 10^{-4} mol.	28	42	57	78
10 10^{-4} mol.	18	24	33	45

No limiting step was detected. However it is difficult to propose any correlation between the concentration in 7 and the yields. In our opinion it is presumably due to the inhibiting effect of acrylamide as shown in the case of acetamide (2). The phenomenon is certainly more complex here because acrylamide is more soluble in water than in the organic phase. Similarly the catalyst should be largely present in the aqueous phase. The transfer phenomenon of the products from one phase to the other one requires further determinations in order to obtain the actual concentrations of all products in each phase.

In conclusion the presence of two phases for the hydration of acrylonitrile by $(Pd(OH)_2(bipy)(H_2O))$ leads to improved yields in acrylamide. The reaction is selective. Further experiments to obtain informations on the mechanism are in progress.

1) Some typical references :

a) V.L. SEALE and R.J. ALLAIN, U.S. Patent 3.928.443
b) J.A. FETCHIN and K.H.Y. TSU, Ger (offen) Patent 2.611.061
c) J.A. FETCHIN and W.F. MARZLUFF, Ger (offen) Patent 2.832.611
d) T. YAMAHARA, T. DEGUCHI and S. NAKAMURA, Jap. Kokaï Patent 76.115.412
e) T. NAKAMURA and Y. OGAWA, Jap. Kokaï Patent 77.79616
f) U.O.P. Inc, Neth (Appl.) Patent 78.00478
g) B. SCHOENBRUNN and V.T. SINHA, Ger (offen) Patent 2.141.662
h) E. SCHOENBRUNN and V.T. SINHA, U.S. Patent 3674 848

2) A. GASET, G. CONSTANT, P. KALCK and G. VILLAIN, J. Mol. Cat. 7, 355 (1980)

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