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NOVEL RHODIUM CLUSTER-CATALYZED REDUCTION OF NITROPROPANE TO PROPIONITRILE UNDER CO AND H_2O

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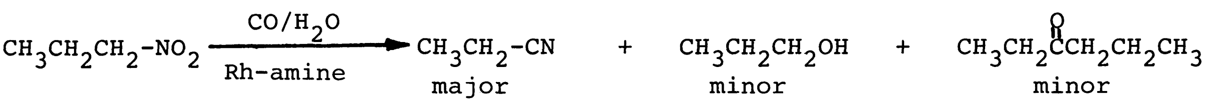
Propionitrile is selectively formed by reduction of nitropropane using CO and H_2O (8 atm of CO, 40 °C). Rhodium carbonyls combined with bases show high catalytic activity. Amines with high pKa values as additives give high yields of propionitrile.

Much attention has been paid on chemical processes using CO and H_2O because the reduction steps can be carried out without use of molecular hydrogen.[1)] We also have studied the water gas shift reaction (WGSR) and its application to organic synthesis using rhodium carbonyl cluster catalysts.[2)] In the reduction of nitrobenzene, a $Rh_6(CO)_{16}$- diamine catalyst system gave aniline in almost quantitative yield, which might be derived from a phenylnitrene intermediate.[3)] In order to compare the reductive reactivity of aromatic nitro compounds with that of aliphatic ones, the reduction of nitropropane using the rhodium catalyst system has been carried out. Unexpectedly, we have found that propionitrile is selectively obtained without formation of propylamine.[4)] To our knowledge,



$$CH_3CH_2CH_2\text{-}NO_2 \xrightarrow[\text{Rh-amine}]{CO/H_2O} \underset{\text{major}}{CH_3CH_2\text{-}CN} + \underset{\text{minor}}{CH_3CH_2CH_2OH} + \underset{\text{minor}}{CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3}$$

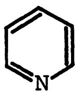
this is the first synthesis of nitrile directly derived from nitro compound using metal catalysts.[5)] Concerning the reduction of aliphatic nitro compounds under WGSR, two examples have been reported; nitropropane is converted to propylamine using the $Ru_3(CO)_{12}$ phase transfer catalyst[6)] and to propionamide using $[Ru(cod)py_4][BPh_4]_2$.[7)]

A general reaction procedure is as follows. Rhodium compound, nitropropane, H_2O, amine, and ethoxyethanol were successively weighed into a glass autoclave. The autoclave (120 ml) was flushed three times with CO and then charged at room temperature to an initial CO pressure of 8 atm. The vessel was heated with stirring at 40 °C. After an appropriate time, gas and liquid phases were analyzed by gas chromatography.

Typical results for this reduction are summarized in Table 1. Propionitrile is a major product accompanying propanol and 3-hexanone. Additive bases were essential for the reduction, which is similar phenomena in rhodium cluster catalyzed-WGSR, -reduction, and -hydrohydroxymethylation.2) Amines with high pKa values were effective as additives and also KOH facilitated the reduction. Water played an important role in the reduction; an increase in the amount of water drastically increased the yield of propionitrile (Runs 11 and 12). The scrutiny of operation conditions reveals that the optimum conditions were 8 atm of CO and 40 °C at the present stage (Run 2).8) Above results are contrast to those for the nitrobenzene reduction; high temperatures above 100 °C are necessary for yielding aniline.2b) Rhodium carbonyl compounds, $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$, and $Rh_2(CO)_4Cl_2$ showed high catalytic activity for the propionitrile formation. In the case of $RhCl_3 \cdot 3H_2O$, the reaction time was prolonged to 48 h for attaining the high yields (Run 8). $RhCl(PPh_3)_3$ was a poor catalyst. Whenever propionitrile was obtained in high yields, the resulting solution became dark green. It is said that increasing the size of rhodium carbonyl cluster anions darkens the color of these solutions.9) The dark green solution indicates that an active species for the propionitrile formation may be Rh_6-Rh_7 carbonyl anions.10) On exposure to air, the solution changed from dark green to brown and IR spectrum of the residue after evaporation of solvent showed bands at 2045 (m), 1962 (s), and 1878 cm^{-1} (m). This spectrum was different from that in the WGSR; an active species for the WGSR had two bands at 1960 and 1805 cm^{-1} characteristic of $[Rh_{14}(CO)_{25}]^{4-}$.2e) The green complex could not be isolated yet.

The mechanism for the reduction is not clear at the present stage. Probably, propylnitrene derived from the reaction of nitropropane with CO may be an intermediate, which is further dehydrogenated to give propionitrile.11) Therefore, requirement of low temperature operation, compared with nitrobenzene, may be due to the course of unstable propylnitrene intermediate. H_2O acts as a reducing agent

Table 1. Reduction of Nitropropane with CO and H_2O Catalyzed by Rhodium Complexes in the Presence of Various Additives[a)]

Run	Catalyst	Additive (pKa)	Product selectivity/%			Conversion/%
			C_2H_5CN	C_3H_7OH	$C_2H_5\underset{O}{\underset{\|}{C}}C_3H_7$	
1	$Rh_6(CO)_{16}$	Et_3N (10.6)	71	27	0	100
2	$Rh_6(CO)_{16}$	A[b)] (10.2)	82	17	0	100
3	$Rh_6(CO)_{16}$	 (5.17)	0	0	0	0
4	$Rh_6(CO)_{16}$	KOH	63	13	2	100[c)]
5	$Rh_4(CO)_{12}$	A	71	19	2	92
6	$Rh_2(CO)_4Cl_2$[d)]	A	80	16	2	96
7	$RhCl_3 \cdot 3H_2O$	A	31	7	1	61
8	$RhCl_3 \cdot 3H_2O$[e)]	A	75	20	2	100
9	$RhCl(PPh_3)_3$	A	78	0	0	7
10[f)]	$Rh_6(CO)_{16}$	A	32	1	2	100[c)]
11[g)]	$Rh_6(CO)_{16}$	A	12	0	2	60[c)]
12[h)]	$Rh_6(CO)_{16}$	A	65	27	0	100

a) Reaction conditions: nitropropane, 5 mmol; Cat., 0.05 mmol; additive, 5 mmol; H_2O, 160 mmol; ethoxyethanol, 2 ml; initial P_{CO}, 8 atm; 40 °C, 24 h.

b) A: N,N,N',N'-Tetramethyl-1,3-propanediamine.

c) A small amount of propionamide ($<$ 5%) was observed but propionic acid could not be detected by gas chromatography.

d) Cat., 0.15 mmol. e) Cat., 0.30 mmol; 48 h.

f) 100 °C. g) Without H_2O. h) H_2O, 40 mmol.

for rhodium compounds to give an active species of rhodium cluster anions.[11)]

An investigation of the scope of the reaction with variety of aliphatic nitrocompounds together with mechanistic investigation is in progress.

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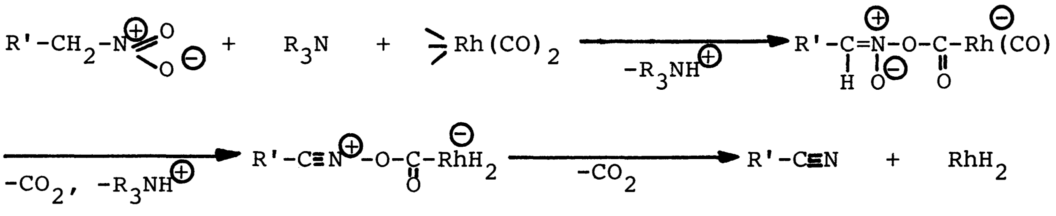

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