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High Deoxygenation Ability of Rh Carbonyl Clusters toward Oximes Leading to Nitrile Formation

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Nitriles are selectively prepared by the reaction of aldoximes with CO and H_2O in the presence of rhodium carbonyl clusters. Rh_{12} and Rh_{13} carbonyl cluster anions can be detected by IR spectroscopy.

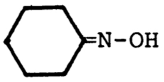
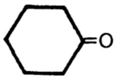
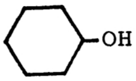
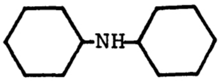
Recently, we have found that the reduction of nitro compounds using CO and H_2O in the presence of rhodium catalysts showed the different reactivity between aromatic and aliphatic nitro compounds; nitrobenzene gave aniline, while nitropropane afforded propionitrile.1,2) This difference may be due to the presence of α-hydrogen in the nitro compounds; nitropropane is reduced to nitrosopropane, which is easily converted into propionaldoxime as a tautomer. Therefore, we have thought that the formed oxime is a key intermediate for the nitrile formation. The reaction of propionaldoxime as a starting material was carried out under the conditions similar to those in the former nitropropane reduction2) and expectedly, propionitrile was obtained in a high yield. Among many nitrile syntheses from oximes,3) this rhodium-catalyzed reaction is unique because dehydration of oximes occurs in aqueous medium with formation of CO_2 and H_2.

$$\text{R-CH=N-OH} \quad + \quad \text{CO} \xrightarrow{Rh_6(CO)_{16}} \text{R-CN} \quad + \quad CO_2 \quad + \quad H_2$$

Table 1 shows the typical examples for the reaction of various oximes. The detectable products are nitriles, alcohols, and ketones. In the course of the reaction, H_2 and CO_2 were generated. Aldoximes except for benzaldoxime give the corresponding nitriles as main products. Ketoximes undergo hydrolysis to give ketones which further are reduced to alcohols. Rhodium compounds are characteristic of this nitrile formation as a catalyst; especially Rh carbonyl clusters have the highest activity. Ru and Fe carbonyl clusters, e.g., $Ru_3(CO)_{12}$ and $Fe(CO)_5$ showed poor catalytic activity under the present reaction conditions. Interestingly, H_2O and basic additives, e.g., diamines and KOH are necessary for attaining high yields of nitriles. Without basic additives, the aldoxime was recovered quantitatively. The reaction solution showed dark green color, which on exposure to air changed to brown slowly. The IR spectrum of the condensed reaction mixture revealed the formation of $[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh_{13}(CO)_{24}H_2]^{3-}$.[4,5]

The reaction of O-alkyl aldoximes did not give the corresponding nitriles. Here, we propose a possible scheme for the nitrile formation which involves nucleophilic attack of $C=N-O^-$ species to the coordinated CO moiety. Specificity of the rhodium catalyst for the present nitrile formation seems to be ascribed to high deoxygenation ability of coordinated carbonyl moiety to rhodium clusters. Oximes are one of the important intermediates in this nitrile formation from nitro compounds.

Table 1. Reaction of Various Oximes with CO and H_2O Using $Rh_6(CO)_{16}$ Catalyst[a)]

Oxime	Products (%, based on oximes used)		
$C_2H_5-CH=N-OH$	C_2H_5-CN (73)	Propanol (12)	
$C_4H_7-CH=N-OH$	C_4H_9-CN (71)	Pentanol (17)	
cyclo-$C_6H_{11}-CH=N-OH$	c-$C_6H_{11}-CN$ (77)	c-$C_6H_{11}-CH_2OH$ (12)	
Ph-$(CH_2)_2-CH=N-OH$	Ph-$(CH_2)_2-CN$ (76)	Ph-$(CH_2)_3OH$ (5)	
Ph-CH=N-OH	Ph-CN (22)	Ph-CH_2OH (46)	
	 (22)	 (12)	 (28)

a) Oxime 5 mmol, $Rh_6(CO)_{16}$ 0.05 mmol, H_2O 2.8 ml, tetramethyl-1,3-propanediamine 5 mmol, ethoxyethanol 2 ml, P_{CO} 8 atm, 40 °C, 5 h.

References

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