APPLICATION OF THE WATER-GAS SHIFT REACTION. REDUCTION OF NITROBENZENES WITH CO AND H2O CATALYZED BY Ru(II) COMPLEXES

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The ionic complex $[Ru(cod)py_4](BPh_4)_2(cod = 1,5-cyclo$ octadiene, py = pyridine) has been shown to be an efficient catalyst for the reduction of nitrobenzenes with carbon monoxide and water, which gives anilines selectively.

Recently many studies on the homogeneous catalysis of the water-gas shift reaction¹ and its application to synthetic reactions² have been reported. In these reactions, one of the important key steps is considered to be a nucleophilic attack of water or hydroxide ion to a metal-bonded carbonyl group^{3,4}. Therefore, increasing the base concentration enhances the activity for those catalyses⁴. On the other hand, the reactivity of the metal-bonded carbonyl groups toward nucleophiles is correlated with the C-O stretching force constants⁵, which are a measure of the positive charge on the carbon atom⁶. This fact suggests that carbonyl ligands coordinated to metal atoms in a high oxidation state are generally more reactive than those in a low oxidation state. Until recently, however, zerovalent metal carbonyls have widely been used in basic solutions as the catalysts for the water-gas shift reaction¹ and its related reactions². It is of interest to find an active catalyst other than zero-valent metal carbonyls without adding bases. This paper deals with the reduction of nitrobenzenes with carbon monoxide and water, which is rarely known^{7,8}.

Surveyed the catalytic activity of complexes of several types, we have found that some Ru(II) complexes are most efficient. Particularly the catalysis of ionic complex, $[Ru(cod)py_{4}](BPh_{4})_{2}^{9}(\underline{1})$, was superior to that of the reported complex, $\operatorname{Ru}_3(\operatorname{CO})_{12}^{7b}$. Other complexes, $\operatorname{AuCl}[P(c-C_6H_{11})_3]$, AgBF_4 , AgOAc, $\operatorname{Cu}(OAc)_2$, PdCl₂(NCPh)₂, FeCl₂py₄, W(CO)₆, and Cr(CO)₆, which were used under the same

conditions, possessed much less activities. In contrast with the catalysis of the ruthenium complexes which converts nitrobenzene into aniline selectively, the palladium-catalyzed reactions gave diphenylurea¹⁰ besides aniline. Diphenylurea appears to be formed by the hydrolysis of phenylisocyanate¹¹, because aniline was not carbonylated under these conditions. The formation of the urea was somewhat suppressed by the addition of zinc chloride or stannous chloride.

$$PhNO_{2} \xrightarrow{CO, H_{2}O} PhNH_{2} \xrightarrow{PhNH_{2}} PhNH_{2} \xrightarrow{PhNH_{2}} PhNH_{2} + PhNHCONHPh$$

We have studied the reduction in detail using the ionic complex (<u>1</u>). The reaction catalyzed by <u>1</u> strongly depended upon the initial pressure of carbon monoxide. We have reduced nitrobenzene (10 mmol) in THF (5 ml) and H_2O (20 mmol) at 100°C for 20 h, using <u>1</u> (0.05 mmol) as catalyst. The respective yields of aniline and carbon dioxide were 36 and 39% (15 atm), 62 and 61% (30 atm), 74 and 73% (45 atm), 90 and 91% (60 atm).

Table l.	Catalytic	Reduction	of	Nitrobenzene	with	со	and	H ₂ 0 '	1)
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Catalyst	Conversion	Product	Products, % yield ^{b) c)}			
	(%) b) c)	Aniline ^{d)}	Diphenylurea ^{e)}	co ₂ d)		
[Ru(cod)py ₄] (BPh ₄) ₂	100 (65)	100 (65)	0 (0)	91 (58)		
RuCl ₂ (CO) ₂ py ₂	100	100	0	92		
RuCl ₂ py ₄	81	81	0	99		
RuH ₂ (PPh ₃) ₄	(34)	(29)	(0)	(29)		
Ru ₃ (CO) f)	(33)	(32)	(0)	(31)		
PdCl ₂ (PPh ₃) ₂	98	38	45	99		
+ ZnCl ₂ g)	96	53	39	87		
+ SnCl ₂ g)	96	65	27	86		
$Pd(PPh_3)_4$	2	2	0	3		
Co ₂ (CO) ₈ h)	10	10	0	3		

a) Conditions: catalyst, 0.2 mmol; nitrobenzene, 20 mmol; H₂O, 40 mmol, THF, 5 ml; initial CO pressure, 50 atm; 145°C, 20 h. The reaction was performed in a 65 ml stainless-steel autoclave.
b) Based on nitrobenzene used.
c) The values in parentheses are the yields obtained at 80°C.
d) GLC yield.
e) Isolated yield.
f) 0.07 mmol.
g) 1.0 mmol.
h) 0.1 mmol.

Substrate	Substituent (X)	Product Yield (%) ^{b)}
	- H	73
NO ₂	p-CH ₃	NH2 89
	p-OCH ₃	56 (100) ^{c)}
	p-Cl	20 (100) ^{c)}
Х	m-CH ₃	73
	m-NO2	44
	<u>o</u> -Ph	71 ^d)

Table 2. Reduction of Substituted Nitrobenzenes Catalyzed by [Ru(cod)py₄](BPh₄)^{a)}

a) Conditions: [Ru(cod)py₄](BPh₄)₂, 0.1 mmol; substrate, 20 mmol; H₂O, 40 mmol;
THF, 5 ml; initial CO pressure, 50 atm; 100°C, 20 h. b) GLC yield.
c) At 170°C. d) At 120°C.

The catalysis of <u>1</u> is applicable to the reduction of substituted nitrobenzenes (Table 2). Nitrobenzenes having electron withdrawing groups were reduced with difficulty, but at 170°C the reduction was complete.

Unlike the $\operatorname{Ru}_3(\operatorname{CO})_{12}$ -N(CH₃)₃ system reported by Pettit et al.^{7b}, complex <u>1</u> itself possessed no catalytic activity for the water-gas shift reaction under the given conditions (CO pressure 15 atm, 100°C). When molecular hydrogen¹², phenol, or methanol was used in place of water, the reduction of nitrobenzene by <u>1</u> did not occur. Neither aniline nor carbon dioxide was formed in the absence of water. Consequently, in the ruthenium-catalyzed reaction the presence of water is essential and this reaction, unlike the palladium catalysis, does not proceed through the intermediary formation of phenylisocyanate. Interestingly, the reduction of <u>0</u>-phenylnitrobenzene gave only <u>0</u>-phenylaniline. The fact that no carbazole is formed also excludes the presence of a nitrene intermediate¹³.

A picture of the overall reaction catalyzed by the Ru(II) complex is given in the Scheme. A similar mechanism has been proposed in the light-assisted watergas shift reaction catalyzed by [RuCl(CO)(bipy)2]Cl¹⁴.



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