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LIGAND EFFECTS IN THE HYDROFORMYLATION OF ACRYLONITRILE BY COBALT CARBONYL

R.A. DUBOIS and P.E. GARROU *

Dow Chemical USA, Central Research – New England Laboratory, Wayland, MA 01778 (U.S.A.)

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Summary

The hydroformylation of acrylonitrile (VCN) using $Co_2(CO)_8/L$ (L = $HN(CH_2CN)_2$, $H_2C(CH_2)_3NMe$, $Me_2N(CH_2)_2NMeH$, PPh_3, and PCy_3) has been examined in methanol solvent. Four reaction pathways are observed which are dependent on L. With no L or with L = $HN(CH_2CN)_2$, the reaction produces the desired acetal $(MeO)_2CHCH_2CH_2CN$. For the more basic amines the reaction produces ~ 50% yields of hydrodimerization products $NCCHMe(CH_2)_2CN$/$NC(CH_2)_4CN$ in a 10/1 ratio and an ~ 30% yield of the hydrogenation product CH_3CH_2CN. These reactions are shown to be metal catalyzed. The main reaction for $Co_2(CO)_8/PR_3$ catalyzed systems appears to be a classical Michael addition reaction of the solvent, methanol, with acrylonitrile to give $MeOCH_2CH_2CN$. Evidence is given to show that this reaction is catalyzed by phosphine which has dissociated under reaction conditions and not by a ligated cobalt complex.

Introduction

The hydroformylation or oxo reaction has for many years been known to be catalyzed in the homogeneous phase by a variety of cobalt compounds all of which produce $HCo(CO)_4$ when exposed to pressures of carbon monoxide [1]. It has also been known that the selectivity and activity of such catalysts can be altered dramatically by the presence of ancilliary ligands such as amines and phosphines [1]. Ono [2], Del'nik [3] and coworkers, have examined the hydroformylation of acrylonitrile (VCN) using $Co_2(CO)_8$ in alcoholic solvents as the catalyst system. To our knowledge no reports on the effect of ancilliary ligands on the Co catalyzed hydroformylation of VCN have been published.

Results and discussion

Detailed examination of the hydroformylation of VCN with Co catalyst systems in alcoholic solvents has revealed the presence of four competitive reaction pathways

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as shown in Fig. 1 and detailed in Table 1. The selectivity to anyone of these products is strongly dependent on the presence or absence of ancilliary ligands. However, in certain instances, the reaction is catalyzed by the ligand, not the ligated cobalt complex.

Pathway 1 describes the normal hydroformylation reaction previously reported using $Co_2(CO)_8$ as catalyst [2,3] which results, due to the alcohol solvent, in the isolation of acetal I as the reaction product. Although previous investigations reported yields of 73–90% at reaction temperatures up to 130°C, we find that the yield of I steadily decreases with increasing temperature so that at 145°C, the selectivity to I has dropped to 42%, and one observes larger quantities of the hydrogenation product, II, the hydrodimerization product, IV, as well as intractable materials. The presence of the aminonitrile $HN(CH_2CN)_2$ (pK_a 0.2) perceptibly increases the stability of the system to temperature (84% yield at 145°C) while minimizing the reaction by alternate pathways 2, and 4 [4]. Increasing the basicity of the amine [$Me_2N(CH_2)_2NHMe$, $CH_2CH_2CH_2CH_2NMe$, pK_a's ~ 10.4] results in the observed products being derived only from pathways 2 and 4.

The hydrodimerization of VCN (pathway 4) has previously been examined using various ruthenium(II) systems [5a,b,c,6,8]. In order to insure that our reactions were metal catalyzed and not simply catalyzed by the nucleophilic amines, blank reactions (Table 1) were run. It was found that VCN + MeOH react at 25°C when catalyzed by *N*-methylpyrrolidine or *N,N,N'*-trimethylethylenediamine to give > 90% yields of methoxypropionitrile, which is the expected Michael addition product. To see if the hydrodimerization would occur if the competition of pathway 3 was not present, we examined the reaction at 130°C in t-butanol [10] and found no conversion after 8 h. Thus, the hydrodimerization appears to be metal catalyzed, and one can envision a mechanism similar to that shown in Fig. 2. Note that the dimerization product, IV, is shown as methyl glutaronitrile which would be obtained by migration of the cyanoethyl group to the internal carbon of a cobalt coordinated VCN. This was the major isomer observed ($NC(CH_2)_4CN/NCCHMe(CH_2)_2CN = 1/10$) by GC and PMR. This branched intermediate must be favored due to steric constraints imposed in the organometallic intermediate. All attempts to isolate such intermediates in this reaction have failed. Examination of the interaction of $Co_2(CO)_8$ with *N*-methylpyrrolidine in MeOH by ^1H, $^{13}C\{^1H\}$ NMR and IR spectroscopy revealed only $Co(MeOH)_6^{2+}[Co(CO)_4^-]_2$. No interaction of the *N*-methylpyrrolidine with $Co_2(CO)_8$ is observed at room temperature under N_2 or 1 atm of CO/H_2 although interaction must be taking place under the reaction conditions in order to alter the direction by which the reaction proceeds.

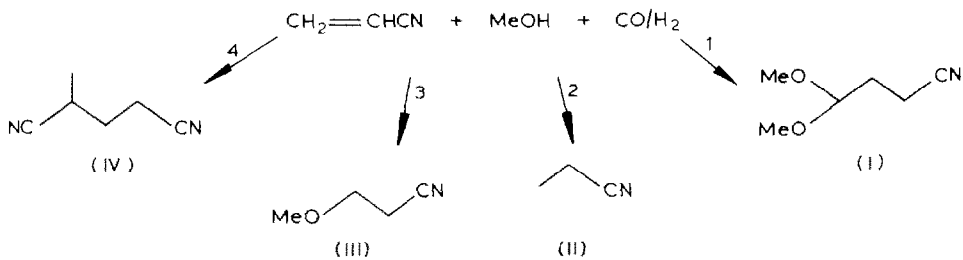
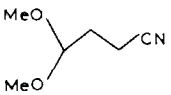
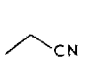
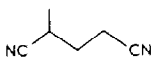
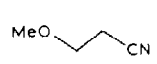
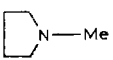


Fig. 1. Observed pathways for the reactions of VCN with CO/H_2 in methanol.

TABLE 1

PRODUCTS FROM THE HYDROFORMYLATION OF ACRYLONITRILE USING MODIFIED COBALT CARBONYL CATALYSTS

Catalyst [a]	T (°C)	pK_a [b]	P(psig)	Time (h)	Conversion (%)	Selectivity (%)			
									
$Co_2(CO)_8$	100		2500	8	100	90	4	2	–
	145					42	17	15	
$[Co(PPh_3)(CO)_3]_2$ [c]	100	2.7	2500	8	< 5	–	–	–	100
	185	2.7	2500	8	100		14 [e]		
$[Co(PCy_3)_2(CO)_3]^+[Co(CO)_4]^-$ [d]	100	9.7	2500	8	30	–	–	–	100
PPh_3	25	2.7	–	2.5	50				100
PCy_3	25	9.7	–	4.5	50				100
$P(Bu)_2Ph$	25	4.2	–	0.3	50				100
$Co_2(CO)_8$ + 2 	130	10.46	2500	8	100	–	30	55	
$Co_2(CO)_8$ + 2 Me_2N–  –NHMe	130	10.40	2500	8	100	–	20	55	
$Co_2(CO)_8$ + 2 $HN(CH_2CN)_2$	100	0.2	2500	8	100	93	3	2	
	145		2500	8	100	84	6	1	
	25	10.46	2500	8	100	–	–	–	> 90
$HN(CH_2CN)_2$	25	0.2	2500	8	0				
 (in t-butanol)	130	10.46	2500	8	0				

[a] In 5 ml MeOH unless otherwise noted, 4×10^{-4} mol cat., 4×10^{-2} mol VCN under 1/1 CO/H_2. [b] Of amine or phosphine. [c] 10 g MeOH + VCN (40.1 mmol) + $[Co(CO)_3PPh_3]_2$ (0.4 mmol). [d] 10 g MeOH + VCN (38.7 mmol) + $[Co(CO)_3(L)_2]^+[Co(CO)_4]^-$ (0.4 mmol). [e] Multitude of other products none > 7%. Internal standard reveals 50% unaccounted for (highers?).

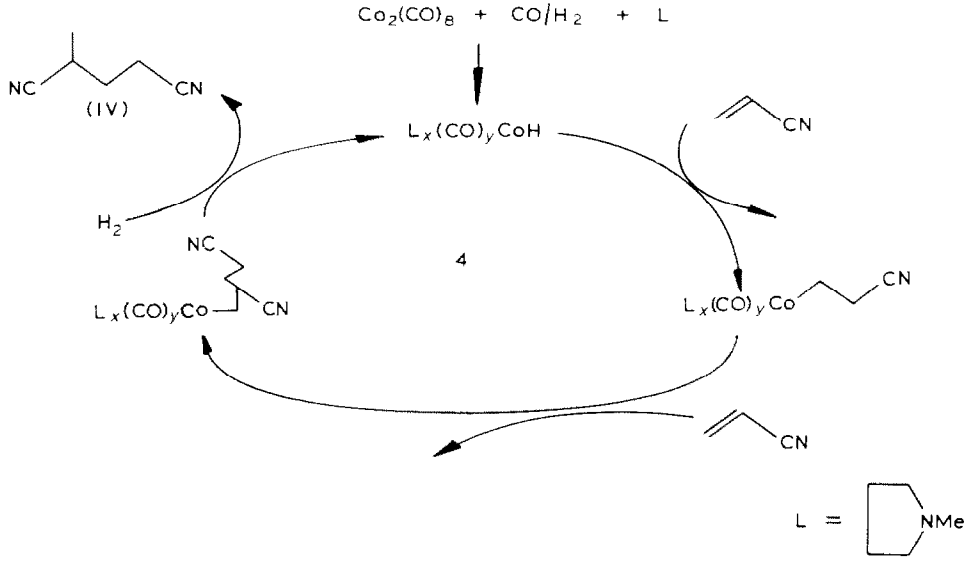


Fig. 2. Catalytic cycle for the dimerization of VCN in methanol.

The main byproduct in these hydrodimerization reactions is the hydrogenated propionitrile, II, which we propose is the result of pathway 2. In this case CO or VCN are not inserted into the cobalt–cyanoethyl bond, but rather the group is reductively eliminated, which regenerates $HCo(CO)_4$. It should be noted that II was the main product identified during the attempted hydrodimerization of VCN using $Co_2(CO)_8$ under a H_2 atmosphere [7].

In contrast to the cobalt carbonyl/amine catalyzed reactions, catalysis by cobalt carbonyl/phosphine catalysts are dependent on the phosphine chosen and the amount of phosphine dissociation that occurs under reaction conditions. Blank reactions (phosphine only) reveal that the reaction is PR_3 catalyzed. Monitoring the conversion of VCN to $MeO(CH_2)_2CN$ (III) by $P(Cy)_3$, PPh_3, and $PPhBu_2$ under

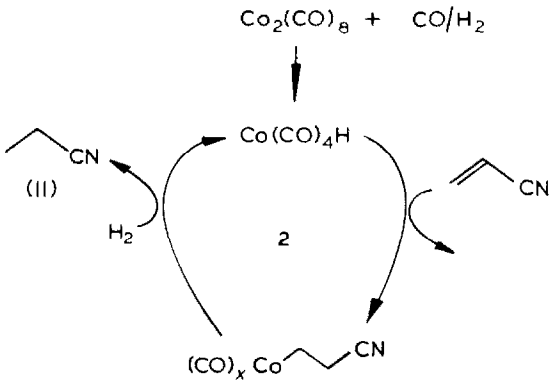
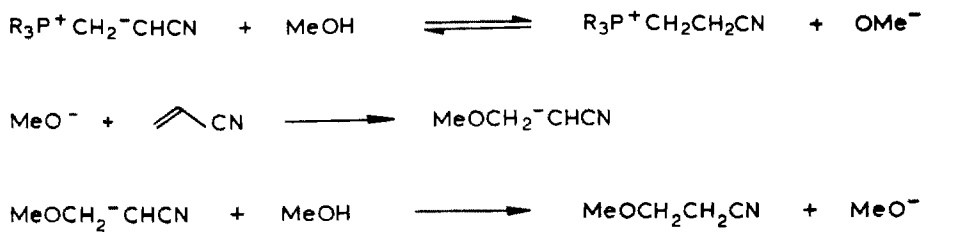


Fig. 3. Catalytic pathway for the hydrogenation of VCN in methanol.

ambient conditions (Table 1) revealed that the relative rates for these phosphines were 1/2/16, respectively. The more basic PCy_3 is the slowest presumably due to steric hindrance. This agrees with earlier findings [12], that nucleophilic phosphines will catalyze the Michael addition of 2-nitropropane to activated olefins. A postulated mechanism would involve R_3P addition to VCN to give the betaine $R_3P^+CH_2^-CHCN$, which then reacts with MeOH as follows:



In contrast to the results of the uncomplexed phosphines, the cobalt complexes $[Co(PCy_3)_2(CO)_3]^+[Co(CO)_4]^-$ and $[Co(PPh_3)(CO)_3]_2$ do not catalyze the Michael addition reaction under ambient conditions, hence we conclude the equilibrium concentration of free phosphine must be minimal.

$$[L_2Co(CO)_3]^+[Co(CO)_4]^- \longleftrightharpoons Co_2(CO)_8 + 2L \rightleftharpoons [Co(CO)_3L]_2$$

In fact, close examination of the $^{31}P\{^1H\}$ NMR of solutions of $[[P(Cy)_3]_2Co(CO)_3]^+[Co(CO)_4]^-$ or $[(PPh_3)Co(CO)_3]_2$ reveals no detectable free ligand signal over the temperature range $+50 \rightarrow -70°C$.

This does not eliminate the possibility of free PR_3 when the solution is under reaction conditions [13]. When the reactions are carried out at 100°C under syn gas, the $P(Cy)_3$ complex (1 mol %) converts 30% of the VCN to III in 8 h whereas the PPh_3 complex effects < 5% conversion. The observation of the Michael addition product and not any hydroformylation product strongly indicate the reaction is being catalyzed by free PR_3 generated under reaction conditions. It is interesting that these Co/PR_3 catalyst systems which are known to be very efficient for normal hydroformylations do not catalyze the hydroformylation of VCN under these conditions. Raising the temperature to 185°C, a more normal temperature for such Co/P hydroformylation systems [1,2] causes extensive decomposition. Only 50% of the starting materials can be accounted for with the highest yield being to the hydrogenation product II, 14%, no other product being present in > 7%.

Conclusions

We have thus observed that the $Co_2(CO)_8$ catalyzed reaction of acrylonitrile with CO/H_2 in methanol is both temperature and ligand sensitive. Addition of $NH(CH_2CN)_2$ produces a hydroformylation system that is more temperature stable, whereas addition of more basic amines results in the inhibition of the hydroformylation reaction and catalyzes hydrodimerization and hydrogenation. Addition of phosphine ligands of various basicities to $Co_2(CO)_8$ catalyzes the Michael addition of methanol to acrylonitrile due to dissociated R_3P. The Michael addition reaction is not catalyzed by a cobalt carbonyl phosphine complex. In conclusion, therefore, four reaction pathways have been observed in the reaction of VCN with CO/H_2 in methanol by the addition of group VA ligands to the basic $Co_2(CO)_8$ catalyst.

Experimental

Unless otherwise indicated all reactions were conducted under purified argon using standard inert atmosphere techniques.

Infrared spectra were recorded on a Beckman 4240 IR Spectrometer. NMR spectra were recorded on a JEOL FX90-Q Spectrometer equipped with a broad band, tunable probe. GLC analyses were performed on a Hewlett–Packard 5730A Gas Chromatograph using a 20% Carbowax/KOH 20M (Chromosorb W) column with tetralin as an internal standard. The temperature programmed mass spectral data was collected using a Hewlett–Packard GC/MS Model 5985 outfitted with a temperature programmed direct insertion probe.

Methanol and VCN were reagent grade and dried with 3A molecular sieves and deoxygenated prior to use. $Co_2(CO)_8$, PCy_3, PPh_3, $PPhMe_2$ and $[Co(CO)_3PPh_3]_2$ were purchased from Strem Chemicals. CH_3CH_2CN, $HN(CH_2CN)_2$, $Me_2N(CH_2)_2NMeH$, $CH_2(CH_2)_2CH_2NMe$, $NC(CH_2)_4CN$, $NCCHMe(CH_2)_2CN$, and $MeO(CH_2)_2CN$ were purchased from Aldrich Chemical. $[Co(PCy_3)_2(CO)_3]^+$-$[Co(CO)_4]^-$ was prepared by standard literature techniques [16].

Hydroformylation (Ex. 1)

$Co_2(CO)_8$ (0.4 mmol) and $HN(CH_2CN)_2$ (0.7 mmol) were added to 5 ml of MeOH in a autoclave liner, in a dry box, and stirred until dissolved. VCN (40 mmol) was then added and the liner transferred to an Aminco rocking autoclave under N_2. The reactor was sealed, purged twice with argon, and pumped up to 2000 psig with CO/H_2. The reaction was heated to 100°C and allowed to rock for 8 h. The reactor was vented and a sample removed. The sample with tetralin (0.25 g) as an internal standard was then analyzed by GLC and mass spectrometry. Analysis of this sample is shown in Table 1. Collection of $(MeO)_2CH(CH_2)_2CN$ on a preparative scale GLC and subsequent PMR analysis verified the assigned structure.

Dimerization / hydrogenation (Ex. 2)

The reaction was run as in Example 1 except that *N*-methylpyrrolidine was substituted for $HN(CH_2CH)_2$. The reaction was worked up and analyzed in a similar manner. Collection of products (CH_3CH_2CN, $NCCHMe(CH_2)_2CN$, $NC(CH_2)_4CN$) by preparative scale GLC and subsequent PMR analysis verified their structural assignments.

Michael addition (Ex. 3)

The reaction was run as in Example 2 except that $Co_2(CO)_8$ was left out and the temperature was held at 25°C. Analysis (GC, mass spectroscopy, PMR) of the reaction product revealed a > 90% yield of $MeO(CH_2)_2CN$.

Attempted Michael addition (Ex. 4, 5)

The reaction was run as in Example 3 except that either $HN(CH_2CN)_2$ was substituted for *N*-methylpyrrolidine or t-butanol was substituted for methanol. Analysis of the reaction revealed no conversion of VCN had occurred.

Michael addition (Ex. 6)

As in Example 1 except $[Co(CO)_3(PCy_3)_2]^+[Co(CO)_4]^-$ (0.4 mmol) 10.0 g MeOH,

2.05 g VCN (38.7 mmol). Analysis of the reaction product revealed 30% conversion of VCN with ~ 100% selectivity to $MeO(CH_2)_2CN$.

Michael addition (Ex. 7)

The reaction was run as in Example 3 except that PCy_3 was substituted for *N*-methylpyrrolidine and there was no CO/H_2 gas pressure. The reaction had a half-life of 4.5 h and produced $MeO(CH_2)_2CN$ with ~ 100% selectivity.

Acknowledgement

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