2,4-Dinitrophenylhydrazone 13 of 2,3-Dimethyl-*N*-formylindole (11).—Concentrated H_2SO_4 (2 drops) was added cautiously to a boiling suspension of DNP (0.1 g) in MeOH (3.5 ml) until a clear solution was obtained, and 11 (86 mg) in MeOH (3 ml) was mixed with it. After the mixture was cooled at 0° for 4 hr, **13** (0.1 g) was collected, crystallized from THF, and obtained as brilliant red, hairy needles: mp 266° dec; ir 1640 cm^{-1} (C=N); mass spectrum (70 eV) *m/e* (rel intensity) 354 (15.90, M + 1), 353 (82.55, M^+), 171 (32.01), 145 (47.13), 144 (100), 143 (34.07), 130 (30.68).

Anal. Calcd for $C_{17}H_{15}N_5O_4 \cdot {}^1/_2(C_4H_8O)$: C, 58.61; H, 4.92. Found: C, 58.75; H, 5.07.

Acknowledgment.—The authors wish to thank Professor A. H. Jackson, University College, Cardiff, Professor D. K. Banerjee, Indian Institute of Science, Bangalore, and Dr. Nitya Nand, Central Drug Research Institute, Lucknow, for recording the nmr and mass spectra.

Registry No.—**1**, 120-72-9; **2**, 948-65-2; **3**, 487-89-8; **4**, 25365-71-3; **5**, 83-34-1; **6**, 91-55-4; **8**, 31951-33-4; **9**, 5257-24-9; **10**, 5257-06-7; **11**, 41601-98-3; **12**, 41601-99-4; **13**, 41602-00-0.

Effect of *p*-Methoxybenzonitrile on the Course of the Stoichiometric Hydroformylation of Cyclopentene

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Received June 29, 1973

The presence of a nitrile, *e.g.*, *p*-methoxybenzonitrile, in the stoichiometric hydroformylation can have a profound effect on both the product distribution and the rate of the reaction. The hydroformylation of cyclopentene under N_2 in the presence of excess $HCo(CO)_4$ produces 52% cyclopentane; the addition of nitrile reduces this to 3% and produces aldehyde almost exclusively. The presence of nitrile retards the rate of hydroformylation when the reaction is conducted under N_2 but accelerates it under CO. These effects are rationalized on the basis of the available concentration of $HCo(CO)_3$ under the various conditions investigated.

In an earlier publication[1] it was shown that, when the stoichiometric hydroformylation of olefins was carried out in the presence of nitriles, the yield of aldehyde was dramatically increased. Thus, under otherwise identical conditions, the addition of 2 mol of PhCN/mol of $HCo(CO)_4$ resulted in an increase of aldehyde yield from 44 to 90%. This high yield, obtained in the presence of a 20-fold excess of olefin, was unexpected because the formation of each mole of aldehyde requires 2 mol of $HCo(CO)_4$ and there were no suggestions in the literature that the final hydrogenolysis step was so fast relative to the earlier $HCo(CO)_4$-consuming steps. Because of these unusual results, we have investigated the nitrile effect more thoroughly and report herewith the results of such studies. Cyclopentene was chosen as a substrate because of its favorable rate of reaction and because double-bond migration does not affect either olefin or aldehyde composition.

Experimental Section

Toluene solutions of $HCo(CO)_4$ were prepared and analyzed according to established procedures.[2] Cyclopentane and cyclopentanecarboxaldehyde were obtained from cyclopentene (Phillips Research Grade) by known catalytic hydrogenation and hydroformylation procedures respectively. Glpc analyses were performed on a Pye Series 105, Model 15, gas chromatograph using a 7 ft × 0.25 in. glass column packed with 25% Carbowax on Chromosorb P. Peak areas were measured with a Disc integrator and were corrected for flame ionization detector response by the use of cyclohexane and mesitylene as internal standards. All reactions were performed at constant temperature (±0.1°) under a static atmosphere.

A typical reaction was conducted as follows. A toluene solution of $HCo(CO)_4$, which had been equilibrated at the desired reaction temperature under CO for 10 min, was syringed into a stirred toluene solution of cyclopentene, cyclohexane, mesitylene, and *p*-methoxybenzonitrile, which had been previously equilibrated under the desired reaction conditions for 10 min. To minimize initial concentration variations, sets of reactions were performed with aliquots from $HCo(CO)_4$ as well as olefin standard stock solutions. At appropriate intervals, 0.2-ml reaction mixture aliquots were withdrawn and quenched by addition to 0.2 ml of a 1.6 *M* toluene solution of triphenylphosphine; all cobalt carbonyl compounds precipitate as insoluble phosphine derivatives. The resulting, clear supernatant was then analyzed by glpc. [The reaction of triphenylphosphine with $HCo(CO)_4$ is extremely fast[3] and the resulting insoluble phosphine complex is unreactive as a hydroformylation catalyst under these conditions.[4]]

Results

Most studies on the stoichiometric hydroformylation have been carried out in the presence of excess olefin. We have followed this practice but, in addition, have also investigated reactions having $HCo(CO)_4$ in excess. The results of both studies are shown in Table I.

The first four reactions reported in Table I were performed in the presence of excess olefin. Reference to these results shows that, in the absence of nitrile, the rate of the reaction is more than 150-fold as fast under N_2 as under CO. Although this effect is well documented in the literature, its magnitude has not been previously defined. The presence of nitrile markedly slows the rate under N_2 but, surprisingly, accelerates it under CO. The yield of aldehyde in both instances is enhanced, as was expected from earlier work.[1]

Similar, but even more striking, results are obtained when the stoichiometric reaction is carried out with hydrocarbonyl in excess. In the absence of nitrile, the major product is cyclopentane regardless of the atmosphere employed. However, in the presence of nitrile, the major product is cyclopentanecarboxaldehyde; cyclopentane formation is negligible. The remarkable ability of *p*-methoxybenzonitrile to increase selectivity to aldehyde and to increase the rate of olefin consumption is brought out by the data shown in graphical form in Figure 1.

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TABLE I
EFFECT OF *p*-METHOXYBENZONITRILE (ArCN) ON THE HYDROFORMYLATION OF CYCLOPENTENE

			Rate[a]		Aldehyde, %[b]		C_5H_{10}, %[b]		C_5H_8, %,[b]
C_5H_8/Co, *M*	Atm	ArCN	10^4k	Rel	1 hr	Final	1 hr	Final	final
12.5[c]	CO	−	1.7	1	1	3[d]	<1	<1[d]	
12.5[c]	CO	+	5.8	3	10	13[e]	<1	1[e]	
12.5[c]	N_2	+	29.6	17	82	84[f]	2	2	
12.5[c]	N_2	−	268.5	158	60	60	10	10	
0.081[g]	CO	−	0.3	1	<1	13[h]	2	34[h]	43
0.066[i]	CO	+	1.2	4	24	77	1	2	24
0.066[i]	N_2	+	3.0	9	47	69	3	3	25
0.066[i]	N_2	−	4.3	13	27	32	48	52	18

[a] Pseudo-first-order rate constants (reciprocal seconds) computed for about 50% cyclopentene disappearance when $HCo(CO)_4$ was in excess and for ~50% of the theoretical amount of product formation when cyclopentene was in excess. [b] Yields: with cyclopentene in excess based on the initial amount of $HCo(CO)_4$ and stoichiometry of 1 mol of product/2 mol of $HCo(CO)_4$; with $HCo(CO)_4$ in excess based on initial cyclopentene concentration. [c] A toluene solution (10.0 ml), 3.11 *M* in cyclopentene, 0.25 *M* in $HCo(CO)_4$, and 0.25 *M* in *p*-methoxybenzonitrile at 10°. [d] Yield at 83 min; after 308 min, 34% aldehyde and 2% cyclopentane. [e] Interrupted after 83 min. [f] Under these conditions at room temperature olefins generally give essentially quantitative aldehyde yields. [g] Cyclopentene (0.0259 *M*). [h] Incomplete after 432 min. [i] A toluene solution (10.4 ml), 0.0212 *M* in cyclopentene, 0.318 *M* in *p*-methoxybenzonitrile, and 0.32 *M* in $HCo(CO)_4$ at 30°.

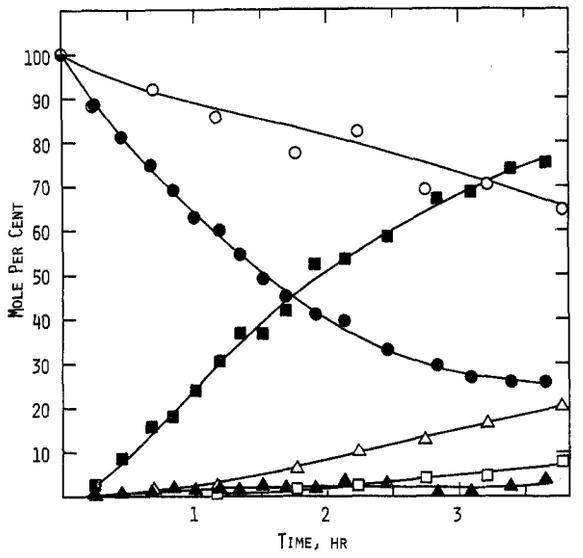

Figure 1.—Stoichiometric hydroformylation of cyclopentene with excess $HCo(CO)_4$ under CO: (○, ●) cyclopentene; (□, ■) cyclopentanecarboxaldehyde; (△, ▲) cyclopentane. Open and solid symbols represent data in the absence and presence of *p*-methoxybenzonitrile, respectively.

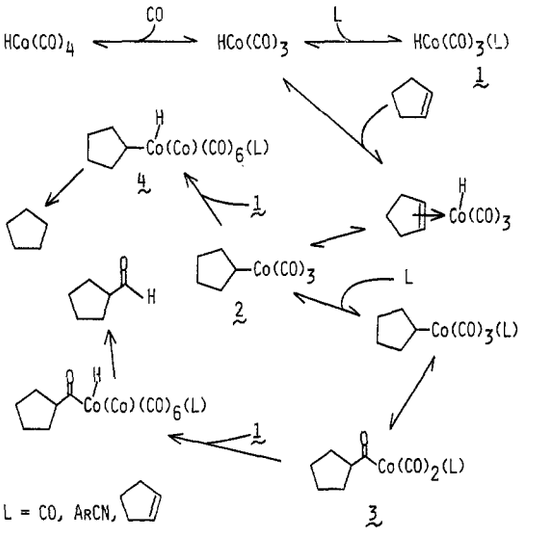

Figure 2.—Stoichiometric hydroformylation and hydrogenation of cyclopentene.

Discussion

The role of nitrile is conveniently analyzed on the basis of two major effects: the effect on product distribution and the effect on rate. Product dependence will be discussed first.

In the catalytic commercial oxo process, olefin hydrogenation is a minor but important undesirable side reaction.[5] In the stoichiometric reaction, especially under N_2 and with low olefin to Co ratios, appreciable hydrogenation occurs.[6] However, from Table I it is seen that the 52% yield of cyclopentane produced under these conditions is reduced to 3% by the addition of nitrile and that practically all of the olefin that is consumed is directed to aldehyde rather than to cyclopentane.

The simplified reaction scheme shown in Figure 2 can be used to rationalize most of our results. The coordinately unsaturated σ complex **2** is shown as a common intermediate. The final products may very well be determined by conditions which affect the partitioning of **2** between the pathways that lead to acyl complex **3** and to the oxidative addition intermediate formulated as **4**. At relatively low nucleophile (CO, nitrile, olefin) concentration, the pathway to cyclopentane is favored. In the absence of nitrile, such conditions prevail when $HCo(CO)_4$ is in excess or are approached when olefin is in excess. In the presence of either excess $HCo(CO)_4$ or excess olefin, the influence of CO on cyclopentane yield is negligible when nitrile is present. This is understandable in view of the very low solubility of CO in toluene at atmospheric pressure ($\sim 6.7 \times 10^{-3}$ *M*)[7] and hence its small concentration relative to that of nitrile (320×10^{-3} *M*, ArCN/CO ≈ 50). The presence of nitrile enhances selectivity to aldehyde under all conditions and this results from the acceleration of the overall rate of alkyl migration[8] which converts **2** to **3**.

We now proceed to analyze the effect of nitrile on the overall rates of reaction. Although nitrile retards the rate of reaction under N_2 (as perhaps might be expected), the fact that it accelerates the rate under CO is difficult to rationalize. Mass balances made in those

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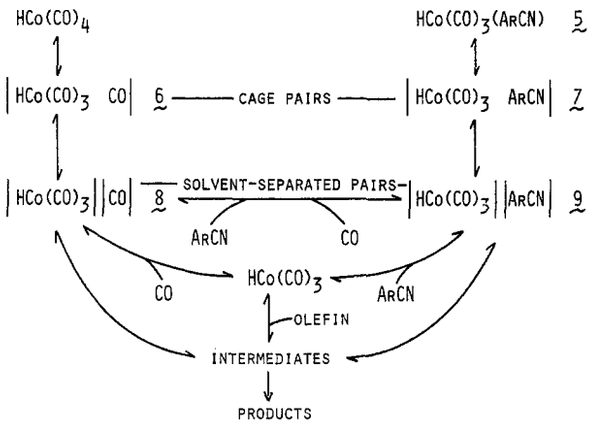

Figure 3.—Solvent cage equilibria.

reactions carried out with excess $HCo(CO)_4$ indicate relatively little accumulation of complexes of any kind (a maximum of 10 mol %), and this accumulation is unaffected by nitrile. These and other considerations lead us to believe that the observed rate differences are not the result of the interaction of nitrile in one of the later or product-determining steps.

The rate of olefin complexation with cobalt hydrocarbonyl as well as subsequent product formation rates should be highly dependent on the concentration of the coordinately unsaturated species $HCo(CO)_3$. The quantity of $HCo(CO)_3$ in equilibrium with $HCo(CO)_4$ under CO at 20° has been estimated to be a few tenths of 1%,[9] and the equilibrium concentration under N_2 is considerably greater.[6b] Thus the well-known, rate-retarding effect of CO[10] is explained on the basis of the suppression of $HCo(CO)_3$ formation, and the presence of nitrile under N_2 should result in a similar suppression and hence in a reduced rate, as in fact it does.

Consideration of reactant concentration changes in bulk solution would lead one to predict that any increase in total nucleophile concentration would reduce the effective concentration of $HCo(CO)_3$ and hence slow the rate of reaction. This is, of course, the effect of high partial pressures of CO in the catalytic reaction. The presence of phosphines in the catalytic reaction is effective in reducing the rate,[11] and the alkyl phosphines are much more effective than the triphenylphosphine in this respect, in accordance with their difference in nucleophilicity. The rate and product distribution is controlled[12] by equilibrium 1. As a matter of fact, the

$$HCo(CO)_4 + R_3P \rightleftharpoons HCo(CO)_3PR_3 + CO \quad (1)$$

position of this equilibrium can be estimated by the product distribution.[12] Our problem is to explain the acceleration of the rate of the stoichiometric reaction under CO when nitrile is added. One possibility is that an increase in the concentration of $HCo(CO)_3$ occurs under these conditions. An analysis based on solvent-cage phenomena may be used for this purpose; the appropriate dissociative equilibria are shown in Figure 3. It is likely that the equilibria between **5**, **7**, and **9** favor the solvent-separated pair to a greater extent than the equilibria between $HCo(CO)_4$, **6**, and **8**; *i.e.*, CO is a better ligand than ArCN. The CO originally present in **8** is lost to solution during the formation of **9**, and hence the effective concentration of $HCo(CO)_3$, either as **9** or as free $HCo(CO)_3$, is higher than in the presence of carbon monoxide alone. The magnitude of this ligand or nucleophile effect should be highly sensitive to the ligating ability of the nucleophile. Too strong a ligand, such as triphenylphosphine, results in the formation of a complex which dissociates hardly at all under the conditions of the stoichiometric reaction, and too weak a nucleophile would give negligible association or rate enhancement. This model suggests that the rate of decomposition of $HCo(CO)_4$, which is also highly sensitive to the effective concentration of $HCo(CO)_3$,[9] should display similar behavior in the presence of *p*-methoxybenzonitrile. The results of just a study confirm this prediction and will be reported separately. A second possible explanation involves the effect of nitrile on the dielectric constant of the solution and the sensitivity of one of the rate determining steps to solvent polarity. The migratory insertion of CO in $Mn(CO)_5$ reactions shows such an effect,[13] and further investigation of this possibility is being explored. Finally, in unpublished work[14] we have established that, under catalytic conditions, nitriles (in particular acetonitrile) have essentially no effect on the course of 1-pentene hydroformylation.

Registry No.—*p*-Methoxybenzonitrile, 874-90-8; cyclopentene, 142-29-0.

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