HYDROFORMYLATION OF FORMALDEHYDE CATALYSED BY RHODIUM COMPLEXES

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Summary

The hydroformylation of formaldehyde to glycol aldehyde ($OHCCH_2OH$) catalysed by rhodium complexes has been studied. The hydrogenation product, methanol, is also formed. The ratio of hydroformylation to hydrogenation is very dependent on the solvent. Hydroformylation is favoured only in N,N-disubstituted amides, with methanol formation predominating in other solvents. This is attributed to the electronic effect of coordinated amide. Complexes of the type $RhCl(CO)L_2$, (L = PPh_3, $P(p\text{-tol})_3$, $P(m\text{-tol})_3$ (tol = tolyl) $P(p\text{-FC}_6H_4)_3$.) are most efficient as catalysts. Deuteration studies show that the mechanism is analogous to that of alkene hydroformylation. A detailed reaction mechanism is proposed.

Introduction

Since its discovery by Roelen in 1938 an enormous amount of work has been carried out on the hydroformylation reaction. Although the reaction of alcohols or epoxides with hydrogen and carbon monoxide has sometimes been classified as hydroformylation [1], the overwhelming proportion of the work has concerned the carbon—carbon double bond. Several reviews of the subject are available [1—4]. Recently a patent issued to Ajinomoto Co. reported the hydroformylation of formaldehyde using cobalt carbonyl as catalyst [5]. Towards the end of this work a second patent on the cobalt catalysed reaction appeared [6]. Here are reported the results of a study of the catalysis of this reaction by rhodium complexes [7].

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Results

The reaction studied is the formation of glycol aldehyde from formaldehyde, hydrogen and carbon monoxide.

$$H_2CO + H_2 + CO \rightarrow HOCH_2CHO$$

As catalyst for the initial work, the complex $RhH(CO)(PPh_3)_3$ [8], which is one of the most effective rhodium catalysts for alkene hydroformylation, was chosen. It was decided first to investigate the solvent dependence of the reaction. Accordingly, conditions of temperature, pressure and concentration typical for alkene hydroformylation were chosen and paraformaldehyde was selected as starting material. The results are given in Table 1. The hydrogenation product methanol was always obtained as a byproduct of the reaction. With $RhH(CO)(PPh_3)_3$ as catalyst the yield of glycol aldehyde was always low, but N,N-dimethylformamide was clearly superior to the other solvents tried. In pyridine several products were formed, but in general only glycol aldehyde and methanol were present in significant quantities. In ethyl acetate and acetonitrile traces of ethylene glycol were formed but in general hydrogenation of glycol aldehyde did not occur.

A series of different types of rhodium complexes was next examined. The results are given in Table 2. The order of catalyst activity does not parallel that found in alkene hydroformylation where for example $RhH(CO)(PPh_3)_3$ is much more active than $RhCl(CO)(PPh_3)_3$ [8]. To investigate further the effect of catalyst structure on the reaction the effect of varying the anionic ligand was studied as reported in Table 3. The chloride complex is clearly superior to the others tried and this was used in further work. Tables 4 and 5 show the effect of temperature and pressure variation. Although the maximum yield of glycol aldehyde occurs at 120°C, the methanol yield is considerably increased and further experiments were carried out at 110°C. The sudden increase in the methanol yield in the range 110—120°C may well be due to thermal elimination of

TABLE 1

SOLVENT DEPENDENCE OF THE HYDROFORMYLATION OF FORMALDEHYDE

Solvent	Glycol aldehyde (%)	Methanol (%)
Acetic acid	0	18.6
Acetone	0	42.0
Acetonitrile	2.8	43.0
Benzene	0	19.7
Dimethylacetamide	5.6	4.1
Dimethylformamide	12.3	4.7
1,4-Dioxane	0	31.7
Ethanol	0	4.2
Ethyl acetate	3.8	63.6
Ethylene glycol	0	24.0
Nitrobenzene	0	6.2
Pyridine	2.8	4.4
Tetrahydrofuran	1.5	52.4

Solvent 100 ml, $RhH(CO)(PPh_3)_3$ 4 × 10^{-3} M, Paraformaldehyde 2 M (in H_2CO), 110°C, 80 atm. H_2-CO (1 : 1), 3 h.

TABLE 2

EFFECT OF CATALYST TYPE ON THE HYDROFORMYLATION OF FORMALDEHYDE

Catalyst	Glycol aldehyde (%)	Methanol (%)
$RhCl(CO)(PPh_3)_2$	23.5	0.4
$RhCl(CO)_2PPh_3$	19.6	0.4
$[Rh(CO_2CH_3)_2PPh_3]_2$	9.8	5.6
$RhH(CO)(PPh_3)_3$	8.5	7.8
$Rh(CO_2CH_3)(CO)(PPh_3)_2$	8.3	20.3
$[Rh(C_8H_{12})(PPh_3)_2]BPh_4$	3.8	26.7
$Rh_4(CO)_{12}$	0	41.8 [a]

Dimethylformamide 100 ml, Catalyst 5×10^{-3} M in Rh, Paraformaldehyde 1 M in H_2CO, 110°C, 80 atm H_2-CO (1 : 1), 3 h.

[a] Rhodium metal formed.

TABLE 3

EFFECT OF VARIATION OF THE ANIONIC LIGAND ON THE HYDROFORMYLATION OF FORMALDEHYDE BY $RhX(CO)(PPh_3)_2$ COMPLEXES

X	Glycol aldehyde (%)	Methanol (%)
Cl^-	23.5	0.4
Br^-	19.0	7.0
I^-	11.0	5.0
NCS^-	9.6	9.0
$CO_2CH_3^-$	8.3	20.3
F^-	5.7	11.3

Dimethylformamide 100 ml, Catalyst 5×10^{-3} M, Paraformaldehyde 1 M in H_2CO, 110°C, 80 atm H_2-CO (1 : 1), 3 h.

TABLE 4

TEMPERATURE DEPENDENCE OF THE HYDROFORMYLATION OF FORMALDEHYDE CATALYSED BY $RhCl(CO)(PPh_3)_2$

Temperature (°C)	Glycol aldehyde (%)	Methanol (%)
95	13.9	0.1
110	23.5	0.4
120	32.0	7.8
125	24.3	8.8
140	13.8	10.3
170	5.6	10.3

Dimethylformamide 100 ml, Catalyst 5×10^{-3} M, Paraformaldehyde 1 M in H_2CO, 80 atm H_2-CO (1 : 1), 3 h.

TABLE 5

PRESSURE DEPENDENCE OF THE HYDROFORMYLATION OF FORMALDEHYDE CATALYSED BY $RhCl(CO)(PPh_3)_2$

Pressure (atm)	Glycol aldehyde (%)	Methanol (%)
80	23.5	0.4
100	32.1	2.1
120	39. 8	2.3
140	43.3	2.3
160	26.6	3.7

Dimethylformamide 100 ml, Catalyst 4×10^{-3} M, Paraformaldehyde 1 M in H_2CO, 110°C, $H_2/CO = 1$, 3 h.

methoxy groups in the paraformaldehyde rather than to hydrogenation. Table 5 shows that pressure affects the glycol aldehyde yield much more than that of methanol, and further experiments were carried out at 120—130 atm pressure.

The effect of varying the phosphine ligand was next studied and the results are given in Table 6. Triphenyl-, tri-p-fluorophenyl- and tri-p- and tri-m-tolyl-phosphines are clearly superior to the others, and the yield of glycol aldehyde falls off steadily with increasing basicity of the phosphine as can be seen in the series triphenyl-, diphenylethyl- and phenyldiethyl-phosphines. Strong π-acceptor ligands such as triphenylphosphite are also of little value as are triphenyl-arsine and triphenylstibine. The effect of adding excess phosphine to the system was also studied in the case of triphenylphosphine (Table 7). Above a phosphine/rhodium ratio of two the hydroformylation is sharply suppressed with an increase in methanol formation.

At this point the solvent dependence was again studied using RhCl(CO)-(PPh$_3$)$_2$ as catalyst under the conditions of Table 6. In dimethylformamide and dimethylacetamide yields of glycol aldehyde of 40—50% were obtained together with a few per cent of methanol. The other solvents used gave no glycol aldehyde formation at all but in most cases methanol was present in moderate yield. This represents an extremely unusual solvent dependence, particularly as the hydroformylation of alkenes can be carried out in almost any solvent [1—4].

Using the conditions given in Table 4 and at 110°C, trioxane and aqueous 37% formaldehyde solution were tried as alternative substrates to paraformaldehyde, at equal total formaldehyde concentrations. No reaction occured with trioxane and no monomer formaldehyde could be detected in the reaction mixture after the experiment, whereas some was always present when paraformaldehyde was used. With aqueous formaldehyde yields of 14% glycol aldehyde

TABLE 6

HYDROFORMYLATION OF FORMALDEHYDE CATALYSED BY RhCl(CO)L$_2$ COMPLEXES

L	Glycol aldehyde (%)	Methanol (%)
P(pCH$_3$C$_6$H$_4$)$_3$	41.0	6.8
P(C$_6$H$_5$)$_3$	39.8	2.3
P(mCH$_3$C$_6$H$_4$)$_3$	37.0	2.6
P(pFC$_6$H$_4$)$_3$	37.0	3.8
P(pCH$_3$OC$_6$H$_4$)$_3$	25.0	9.6
P(CH$_2$C$_6$H$_5$)$_3$	16.0	5.0
P(C$_6$H$_5$)$_2$C$_2$H$_5$	11.9	5.6
P(C$_6$H$_{11}$)$_3$	9.0	2.5
P(p(CH$_3$)$_2$NC$_6$H$_4$)$_3$	8.2	7.8
PC$_6$H$_5$(C$_2$H$_5$)$_2$	4.6	10.0
P(nC$_4$H$_9$)$_3$	3.7	4.8
P(oCH$_3$C$_6$H$_4$)$_2$	2.2	9.0
P(OC$_6$H$_5$)$_3$	2.0	13.0
P(C$_6$F$_5$)$_3$	0	0
As(C$_6$H$_5$)$_3$	0.5	0
Sb(C$_6$H$_5$)$_3$	0	1.2

Dimethylformamide 100 ml, Catalyst 5 × 10^{-3} M, Paraformaldehyde 1 M in H$_2$CO, 110°C, 120 atm H$_2$-CO (1 : 1), 3 h.

TABLE 7

EFFECT OF TRIPHENYLPHOSPHINE OF THE HYDROFORMYLATION OF FORMALDEHYDE

Ratio P/Rh	Glycol aldehyde (%)	Methanol (%)
1 [a]	19.6	0.3
2	23.5	0.4
5	5.0	5.0
10	4.0	10.0
50	0	14.4

Dimethylformamide 100 ml, $RhCl(CO)(PPh_3)_2$ 5×10^{-3} M, Paraformaldehyde 1 M in H_2CO, 110°C, 80 atm H_2-CO (1 : 1), 3 h.
[a] $RhCl(CO)_2(PPh_3)$ as catalyst.

and 39% methanol were obtained and paraformaldehyde was therefore used in all further experiments. The effect of variation of amide structure is shown in Table 8. It is essential that the nitrogen atom be disubstituted and the yield of glycol aldehyde may be reduced if excessively large groups are present. Larger groups may be permissible on the nitrogen atom provided only one of them is present. Although the best yield obtained was in dimethylacetamide, form-amides were preferred as the use of other amides led to 2—5% of the corre-sponding formamide being produced in the reaction. This may be due either to reaction of the amides with formaldehyde or to cleavage of the N—CO bond followed by carbonylation of the resulting diamine to the formamide. This reaction did not occur with N-methylpyrrolidone.

Table 9 shows the effect of variation of the catalyst and substrate concentra-tions using dimethylacetamide as solvent. In both cases the glycol aldehyde yield is little affected over a wide concentration range. The formation of meth-anol can be completely suppressed without significant reduction in the glycol aldehyde yield. The gas uptake in the reaction had normally ceased after $2\frac{1}{2}$ hours. In dimethylformamide no increase in glycol aldehyde yield was observed on extending the reaction time to 5 hours. Since the reaction ceases at a form-

TABLE 8

HYDROFORMYLATION OF FORMALDEHYDE BY $RhCl(CO)(PPh_3)_2$ IN AMIDE SOLVENTS

Solvent	Glycol aldehyde (%)	Methanol (%)
H_2NCHO	0	0
$H(CH_3)CHO$	0	0
$(CH_3)_2NCHO$	39.8	2.3
$(C_2H_5)_2NCHO$	48.6	2.6
$(nC_3H_7)_2NCHO$	29.6	5.2
$(nC_4H_9)_2NCHO$	26.6	4.7
$CH_3(C_6H_5)NCHO$	0	0
$CH_3(C_6H_{11})NCHO$	14.7	1.8
$CH_3(C_6H_5CH_2)NCHO$	42.7	8.6
$(CH_3)_2NCOCH_3$	49.7	1.2
$(CH_3)_2NCOC_2H_5$	31.1	3.1
$(C_2H_5)_2NCOCH_3$	27.2	3.8
$CH_3NCOCH_2CH_2CH_2$	40.9	2.1

Solvent 100 ml, Catalyst 5×10^{-3} M, Paraformaldehyde 1 M in H_2CO, 110°C, 130 atm H_2-CO (1 : 1), 3 h.

TABLE 9

EFFECT OF VARIATION OF CATALYST AND FORMALDEHYDE CONCENTRATIONS ON THE HYDROFORMYLATION OF FORMALDEHYDE

Catalyst (M)	Formaldehyde (M)	Glycol aldehyde (%)	Methanol (%)
5×10^{-3}	2	44.7	3.4
5×10^{-3}	1	49.7	1.2
5×10^{-3}	0.5	47.1	0
5×10^{-3}	0.25	35.0	0
5×10^{-3}	0.125	26.7	0
1.25×10^{-3}	1	44.7	1.4
2.5×10^{-3}	1	47.9	1.2
5×10^{-4}	1	49.7	1.2
12.5×10^{-3}	1	47.8	0.9
25×10^{-3}	1	26.9	2.6

Dimethylacetamide 100 ml, RhCl(CO)(PPh$_3$)$_2$ and substrate as shown, 110°C, 130 atm H$_2$-CO (1 : 1), 3 h.

aldehyde conversion of at most 50% the cause of this evident inhibition of the reaction was sought. The possibilities of inhibition by glycol aldehyde or by diamine formed by decarbonylation of the solvent were investigated. The effect of adding glycol aldehyde to the system is shown in Figure 1. It can be seen that strong inhibition occurs, with a maximum glycol aldehyde yield of ca. 42%. Although very low concentrations of dimethylamine are formed during this reaction, it was found that much higher concentrations were necessary to affect the reaction significantly. Glycol aldehyde appears therefore to be the sole cause of the inhibition.

In connection with the mechanism of the reaction, separate experiments were carried out using a carbon monoxide-deuterium gas phase, para(formaldehyde-d_2) and dimethylformamide-d_7. In each case the glycol aldehyde was iso-
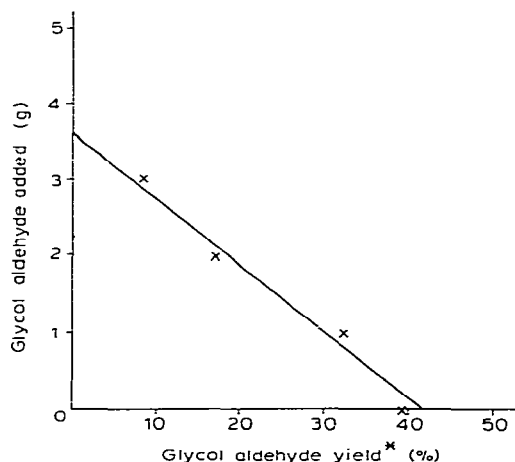

Fig. 1. Effect of added glycol aldehyde on the hydroformylation of formaldehyde. Dimethylformamide 100 ml, RhCl(CO)(PPh$_3$)$_2$ 5 × 10^{-3} M, Paraformaldehyde 1 M in H$_2$CO, 110°C, 130 atm H$_2$-CO (1 : 1). 3 h.* Total glycol aldehyde less that added at start.

lated and its ^1H NMR spectrum was recorded in D_2O to determine the distribution of deuterium over the carbon atoms, the alcohol proton having of course exchanged with the D_2O. Glycol aldehyde in the solid state, in dimethylformamide and in strong aqueous solution exists as the dimer, 2,5-dihydroxy-1,4-dioxane [9]. The ^1H spectrum of the dimer is extremely complicated but dilute D_2O solutions show the expected doublet-triplet spectrum of the monomer. When a $CO-D_2$ gas phase was used, the NMR spectrum showed $ODCCH_2OD$ present. Using para(formaldehyde-d_2) $OHCCD_2OD$ was formed and in dimethylformamide-d_7, $OHCCH_2OD$ was found.

Discussion

The deuteration experiments show clearly that the mechanism of the hydroformylation of formaldehyde is entirely analogous to that of alkene hydroformylation. In view of this it is most surprising that the reaction occurs only in N,N-disubstituted amides, since alkenes may be hydroformylated in almost any liquid phase [1—4]. Such specificity can hardly be attributed to the presence of solvent in the outer coordination sphere of the catalyst alone and the absence of deuterium in the product when dimethylformamide-d_7 was used as solvent rules out the possibility that the solvent plays an active role in the reaction via for example the formyl group. It therefore appears that the solvent must function as a ligand in at least one stage of the catalytic cycle. Since it is hard to envisage the beneficial effect of coordinated amide being steric in nature particularly as a wide range of amides is useful, it must be assumed that the effect is electronic. The behaviour of N-methyl-N-cyclohexylformamide and N-methyl-N-phenylformamide supports this view (Table 8). The absence of any glycol aldehyde formation in the latter solvent is attributed to disturbance of the electronic structure of the formamide unit by delocalisation of the lone-pair of the nitrogen atom over the phenyl group. The effect of variation of size of the substituents on the nitrogen atom can be explained as a steric effect on coordination of the amide to the catalyst. Table 8 shows that both for the nitrogen and carbonyl-carbon atoms the presence of groups larger than ethyl may reduce the glycol aldehyde yield. There is at present relatively little known about the coordination of amides to transition metals but it is clear that the coordination occurs through the oxygen atom both for rhodium and for other metals [10]. The amide unit is planar at room temperature due to resonance:
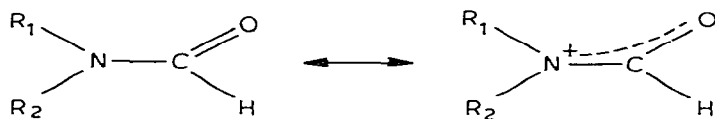
NMR studies have shown that free rotation about the C—N bond commences, at 119°C for dimethylformamide [11]. The nitrogen substituent which is *cis* to the oxygen atom would therefore make the dominant contribution to the steric hindrance of coordination. A formamide containing two different groups on the nitrogen atom might then be able to coordinate where a symmetrically substituted formamide would be hindered. This does appear to be the case as can

be seen by comparing *N,N*-di-n-butylformamide and *N*-methyl-*N*-benzylform-amide, both of which have the same number of carbon atoms (Table 8). Table 1 shows that the solvent alone can markedly affect whether hydroformylation or hydrogenation occurs. There are three ways in which a coordinated amide might bring this about. Firstly it could affect the mode of addition of formaldehyde to the Rh—H bond.

$$\begin{array}{ll} \text{Rh—H} \nearrow (\text{Rh—CH}_2\text{OH}) \rightarrow & \text{Glycol aldehyde} \\ \text{H}_2\text{C}\!=\!\text{O} \searrow (\text{Rh—OCH}_3) \rightarrow & \text{or methanol} \\ & \text{Methanol or} \\ & \text{methyl formate} \end{array}$$

Methyl formate was never present in more than trace quantities. The presence of a hydroxymethyl intermediate is required for glycol aldehyde production. Whether the methanol formed in amide solvents is formed by this route or by the methoxide route or both is not known, but direction of the reaction via the hydroxymethyl route in amide solvents could explain the specificity. A second possibility is that an amide ligand facilitates the attack of the hydroxy-methyl group on coordinated carbon monoxide to produce the acyl species Rh—COCH$_2$OH. The third possibility which assumes that the preceeding steps are reversible is that the amide favours the elimination of glycol aldehyde from the acyl-hydride rather than methanol from a hydroxymethyl- or methoxide-hydride.

The inhibition of hydroformylation by excess triphenylphosphine and the reduced glycol aldehyde yield when aqueous formaldehyde was used also support the idea of amide coordination, since both triphenylphosphine and water could coordinate preferentially to the metal. The mechanism proposed for the reaction is summarised in Scheme 1 and is discussed further below.

Analysis of the reaction mixtures showed that monomer formaldehyde was already present when paraformaldehyde was used as substrate, as would be expected from the low conversion and the known thermal depolymerisation of paraformaldehyde [12]. The catalysis is expected to involve this monomer rather than attack of a rhodium hydride on the polymer chain. The absence of any reaction with trioxane is attributed to its stability under the reaction conditions, no monomer being detected after such reactions.

The product inhibition shown in Figure 1 is to be expected since both substrate and product are aldehydes and will therefore compete for the catalyst. Glycol aldehyde may further be capable of acting as a bidentate ligand.

A detailed mechanism for the reaction is given in Scheme 1. From the results of Table 2 it is apparent that the chloride ligand is not displaced as in alkene hydroformylation [13] since if this were so the differences shown in the Table would not be expected. Further, up to 75% of the catalyst could be isolated after the reaction as RhCl(CO)(PPh$_3$)$_2$. The dissociation of one of the phosphine ligands probably occurs. The other positions at the metal would then be occupied by hydrogen, carbon monoxide, the solvent and the substrate, though the presence of bisphosphine species cannot be ruled out. Dicarbonyl species of rhodium(I) will almost certainly be present in the reaction mixture but since

SCHEME 1 [a]

PROPOSED MECHANISM FOR THE HYDROFORMYLATION OF FORMALDEHYDE

L = amide

[a] Except for *cis*-orientation of reacting groups, stereochemistry is arbitrary. Dicarbonyl species omitted.

they should be incapable of activating hydrogen they would play no role in the actual catalysis and they are therefore omitted from the Scheme. In view of the very poor π-bonding ability of aldehydes, hydrogen activation is expected to precede formaldehyde coordination, which may occur via an initial σ-bonded form, bonding through the oxygen atom. Except for the *cis*-orientation of reacting groups, the stereochemistry about rhodium represented in the Scheme is arbitrary.

Although oxidative addition of hydrogen possibly occurs in both mono- and bis-phosphine species, complex V must be a key intermediate in the reaction. This does not contain coordinated amide, but the solvent could still affect the further reaction of V since it is present in both VIII and VI. This again assumes that the appropriate reactions are reversible, which is not known with certainty. If the effect of the amide is limited to a single step of the reaction, then the formation of the acyl species, VI→VII, appears the most likely.

Experimental

Gas chromatographic analyses were obtained with a Varian Aerograph series 1700 instrument using an Infotronics CRS-104 integrator and calibrated using internal standards. Samples were silylated with RC 2 reagent from Regis Chemical to facilitate the analysis for Glycol aldehyde. Infra-red and ^{1}H NMR spectra

were recorded using Beckman IR 12 and Varian T-60 instruments, respectively.

$RhCl_3 3 H_2O$ and $Rh_2Cl_2(CO)_4$ were obtained from Matthey-Bishop and Strem Chemical. Phosphines were obtained from Strem and Aldrich. RhCl-$(CO)L_2$ complexes (L = phosphine, arsine, stibine) were prepared from either $RhCl_3 3 H_2O$ [14] or $Rh_2Cl_2(CO)_4$ [15]. The following complexes were prepared according to the given literature methods: $RhCl(CO)_2PPh_3$ [16], Rh_2-$(CO_2CH_3)_4(PPh_3)_2$ [17], $RhH(CO)(PPh_3)_3$ [18], $Rh(CO_2CH_3)(CO)(PPh_3)_2$ [19], $[Rh(C_8H_{12})(PPh_3)_2]BPh_4$ [20], $Rh(NCS)(CO)(PPh_3)_2$ [21], $RhBr(CO)(PPh_3)_2$ [21], $RhF(CO)(PPh_3)_2$ [22], $RhI(CO)(PPh_3)_2$ [23].

Products were checked by their infra-red spectra and the bromide and iodide, which were prepared by halide exchange, were analysed for halide. Glycol aldehyde was from Aldrich. Simple amides and other solvents were from Fisher or Mallinckrodt. Other amides were prepared from acid and amine by the toluene method [24].

Hydroformylation

Except for the experiment in dimethylformamide-d_7, all autoclave experiments utilised a 300 ml Magnedrive autoclave of stainless steel or Hasterlloy B, fitted with a Dispersimax stirrer, cooling coils, temperature probe and constant pressure attachment. The catalyst was sealed in a glass bulb under argon for addition to the autoclave. The autoclave was heated to the reaction temperature under 1 atm H_2-CO (1 : 1). All pressures quoted are those at the reaction temperature. Reaction mixtures were analysed gas chromatographically on Carbowax 20M and VCW 98 columns in the latter case after silylation (above). For the dimethylformamide-d_7 experiment the reaction was carried out on a 10 ml scale under the conditions of Table 2 using $RhCl(CO)(PPh_3)_2$ as catalyst at a pressure of 70 atm. A 45 ml stainless steel rocking autoclave was used. The experiments with para(formaldehyde-d_2) (Merck) and deuterium-carbon monoxide (Matheson) were also carried out as in Table 2 using the same catalyst. The gas phase was analysed for H_2, HD and D_2 by mass spectrometry.

References

1 J. Falbe, Synthesen mit Kohlenmonoxid, Springer-Verlag, Berlin, 1967. pp. 3—72.
2 L. Markó in R. Ugo (Ed.) Aspects of Homogeneous Catalysis, Riedel, Dordrecht, Holland, 1974. pp. 3—55.
3 F.E. Paulik, Cat. Rev., 6 (1972) 49.
4 F. Asinger, Die Petrochemische Industrie, Akademie-Verlag, Berlin, 1971, pp. 1122—1174.
5 Ajinomoto Co. (1975) US Patent 3,920,753.
6 Mitsubishi Co. (1976), Jap. Patent 51 (1976) 128,903.
7 Monsanto Co. (1977) Eur. Patent 0,002,908
8 C.K. Brown and G. Wilkinson, J. Chem. Soc. A, (1970) 2753.
9 G.C.S. Collins and W.O. George, J. Chem. Soc. B, (1971) 1352.
10 R.S. Drago, R.L. Carlson and K.F. Purcell, Inorg. Chem., 4 (1965) 15; W.E. Bull, S.K. Madan and J.E. Willis, Inorg. Chem., 2 (1963) 303; P. Abley and F.J. Mcquillin, Chem. Commun., (1969) 477.
11 M. Rabinovitz and A. Pines, J. Amer. Chem. Soc., 91 (1969) 1585; T. Drakenberg, K-L. Dahlquist and S. Forsén, J. Phys. Chem., 76 (1972) 2178.
12 J.F. Walker, Formaldehyde, 2nd Edition, Reinhold, New York, 1953.
13 D. Evans, J.A. Osborn and G. Wilkinson, J. Chem. Soc. A, (1968) 3133.
14 D. Evans, J.A. Osborn and G. Wilkinson, Inorg. Synth., 11 (1968) 99.
15 J.A. McCleverty and G. Wilkinson, Inorg. Synth., 8 (1966) 214.
16 G. Deganello, P. Uguagliati, B. Crociani and U. Belluco, J. Chem. Soc. A, (1969) 2726.

17 P. Legzdins, R.W. Mitchell, G.L. Rempel, J.D. Ruddick and G. Wilkinson, J. Chem. Soc. A, (1970) 3322.

18 D. Evans, G. Yagupsky and G. Wilkinson, J. Chem. Soc. A, (1968) 2660.

19 A. Spencer, J. Organometal. Chem., 124 (1977) 85.

20 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 93 (1971) 2397.

21 J. Chatt and B.L. Shaw, J. Chem. Soc. A., (1966) 1437.

22 L. Vaska and J. Peone, Jr., Chem. Commun., (1971) 418.

23 L. Vallarino, J. Chem. Soc., (1957) 2287.

24 L.F. Fieser and J.E. Jones, Org. Synth., 20 (1940) 66.