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THE MECHANISM OF PHOSPHINE-MODIFIED RHODIUM-CATALYZED HYDROFORMYLATION STUDIED BY CIR–FTIR

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Summary

The mechanism of phosphine-modified rhodium-catalyzed hydroformylation of 1-hexene was studied by *in situ* infrared spectroscopy using high pressure autoclaves equipped with embedded cylindrical internal reflectance crystals (CIR–FTIR). A series of $RhH(CO)_2(PR_3)_2$ complexes 1 were synthesized using *p*-substituted triarylphosphines where the electron density on rhodium was varied by using *p*-$N(CH_3)_2$, *p*-OCH_3, *p*-H, *p*-F, *p*-Cl or *p*-CF_3. The metal carbonyl and metal hydride infrared stretching frequencies were correlated by a standard Hammett treatment of the data. Reaction rates and selectivities for linear aldehydes both increased with increasingly electron-withdrawing phosphines. The IR spectra, measured under autogenous conditions of 70 °C and 200 psi (1.38 MPa), showed the presence of various intermediates in the catalytic cycle depending upon the phosphine modification, P/Rh ratio, total syngas pressure, and degree of olefin conversion.

The rate and spectroscopic data permitted the assignment of a reaction mechanism involving CO dissociation from $RhH(CO)_2L_2$ 1 as the primary selective hydroformylation pathway.

Introduction

The hydroformylation reaction was discovered by Roelen [1] in 1938 using a heterogeneous cobalt catalyst, and has evolved into commercial processes operating at high pressure using both cobalt carbonyl [2] and phosphine-coordinated cobalt carbonyl [3] catalysts. The reaction was reviewed by several authors [4 - 7] and is shown schematically below.

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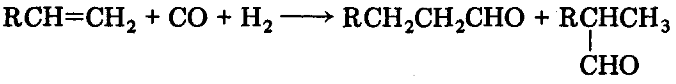


$$RCH{=}CH_2 + CO + H_2 \longrightarrow RCH_2CH_2CHO + R\underset{\underset{\displaystyle CHO}{|}}{C}HCH_3$$

linear 2

branched 3

Hydroformylation processes using low pressure rhodium phosphine catalysts were first investigated by Slaugh and Mullineaux of Shell [8] and Eisenman of Diamond Alkali [9] in 1966. Wilkinson and co-workers [10 - 14] examined the coordination chemistry of several rhodium complexes which were potential intermediates in this process, and proposed a reaction mechanism [13] which has been generally favored.

This report provides evidence for a new mechanism for the phosphine-modified rhodium-catalyzed hydroformylation of olefins using a new FTIR technique which was recently reported [15 - 18], based on *in situ* analysis in high pressure autoclaves equipped with cylindrical internal reflectance (CIR) crystals.

Recent studies [15] have shown that high pressure CIR–FTIR analyses of a variety of homogeneous [16] and heterogeneous catalyzed reactions [17] afforded high quality spectra of the intermediates in these reactions. The method was shown to be especially suited for examining the course of organic reactions, zeolite syntheses and other hydrogel preparations, and solid–liquid slurry reactions [18]. The advantage of this technique for mechanistic studies of hydroformylation is its facility in obtaining high pressure analyses where the analyzing crystal is directly in contact with the well-stirred gas–liquid zone of the reactor. The method permits the acquisition of kinetic data while the concentrations of intermediates are monitored.

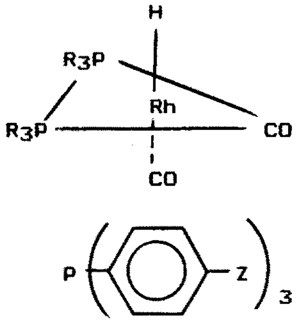
High pressure *in situ* infrared studies were previously carried out on the phosphine-modified rhodium system by Morris and Tinker [19] and by Wilkinson and co-workers [20] using IR transmission cells where the reacting solution was periodically flowed from a high pressure autoclave into an externally located IR cell. These studies were unable to provide evidence to support the proposed mechanisms, principally due to the inability of the equipment to provide steady state reactor analysis under autogenous conditions. Since rates and product distributions are sensitive to reaction parameters [14], it is important that mechanistic studies be carried out under representative hydroformylation conditions.

The rhodium-catalyzed hydroformylation reaction mechanism proposed by Evans and co-workers [13] suggested that the selective reaction producing the linear aldehyde 2 resulted from an ‘associative’ reaction cycle, and that the branched aldehyde 3 resulted from an independent ‘dissociative’ cycle where an important step in the mechanism was the dissociation of a phosphine ligand. A recently proposed mechanism by Unruh, Christenson and Hughes [21, 22] based on NMR data provided evidence that a key intermediate, $RhHL_3$, was involved in the selective process forming the linear aldehyde 2. The mechanistic studies reported here were prompted by the development of the CIR–FTIR reactors which made high quality *in situ* analyses readily available, and by hydroformylation data in the literature which could not be rationalized by the previously proposed Wilkinson mechanism.

Results and discussion

An examination of several literature studies [5 - 7] shows apparent discrepancies with respect to the effect of several process parameters on activity, selectivity and kinetic order in rhodium-catalyzed hydroformylation. For example, the rate expressions obtained by Marko and co-workers [23] showed widely differing kinetic orders for olefin, catalyst, H_2 and CO when the substrate was changed from 1-hexene to cyclohexene. These differences and others are likely due to a mechanistic scheme composed of transformations having similar rates, rather than entirely different reaction mechanisms. To avoid this particular difficulty in analyzing activity data, a model system was selected where the steric requirements of the reacting molecules remained nearly constant while the electron distribution was gradually modified by phosphine substitution.

A series of trigonal bypyramidal complexes 1, $RhH(CO)_2(PR_3)_2$ (shown in Fig. 1), were prepared using the substituents indicated. The metal hydride and metal carbonyl IR stretching frequencies for these complexes were



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Z	Infrared frequencies	
	metal hydride	metal carbonyls
$-N(CH_3)_2$	2018	1957, 1918
$-OCH_3$	2033	1976, 1930
$-H$	2039	1981, 1937
$-F$	2041	1988, 1947
$-Cl$	2042	1991, 1948
$-CF_3$	2050	1997, 1953

Fig. 1. Trigonal bipyramidal complexes prepared *in situ* at room temperature under 160 psi (1.10 MPa) of 1:1 H_2/CO in dichloroethane. IR frequencies (cm^{-1}) are given for the rhodium hydride and carbonyl stretching bands.

measured and correlated by a Hammett treatment, which showed that the electron density at the metal could be controlled in a predictable way. The complexes were then reacted with 1-hexene under a variety of conditions in syngas atmospheres; their reaction rates were measured and steady state intermediates were observed *in situ* under autogenous conditions.

Electronic effects in prepared catalysts

The series of complexes shown in Fig. 1 were synthesized in dichloroethane at room temperature under a 1:1 H_2/CO atmosphere at a pressure of 160 psi (1.10 MPa). All of the trigonal bipyramidal complexes were prepared starting with 1 equiv of $Rh_4(CO)_{12}$ and 24 equiv of PR_2, yielding solutions of the complex having a four-fold ligand excess. A typical IR spectrum for the triphenylphosphine derivative is shown in Fig. 2, measured on a stirred solution under syngas pressure. Under these conditions the metal hydride frequency appeared at 2038 cm^{-1}; the two metal carbonyl stretching frequencies were at 1981 and 1936 cm^{-1}. Depending on the phosphine ligand, the room temperature spectra also indicated the presence of various amounts of the yellow dimer 4, $[Rh(CO)_2L_2]_2$, reported previously [14]; one band of this species is clearly seen in Fig. 2 at 1772 cm^{-1}, assigned to the bridging carbonyl group. In contrast to prior NMR data which reported varying equilibrium concentrations of $RhH(CO)L_2$ depending on solvent, temperature and conditions, our IR data obtained at PR_3/Rh ratios of 6:1 show no evidence for this species which is reported [12] to absorb at 2000 and 1920 cm^{-1}. An examination of the curve-resolved IR spectrum after mixing $Rh_4(CO)_{12}$ and PR_3 under nitrogen, prior to syngas pressurization, showed bands for the yellow dimer 4, the orange dimer 5, and solvated red dimer 6 previously reported by Wilkinson and co-workers [12, 14]. The structure of these dimers may be seen in Fig. 3. A curve-resolved IR spectrum for this

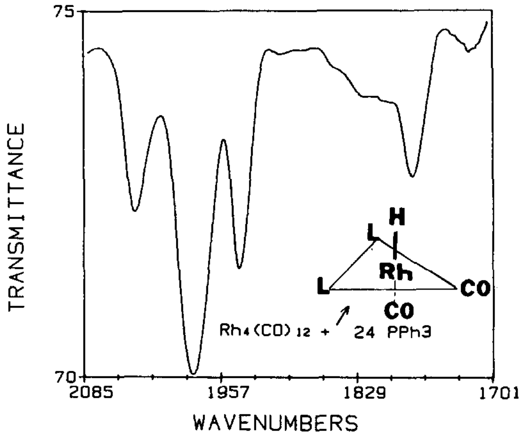
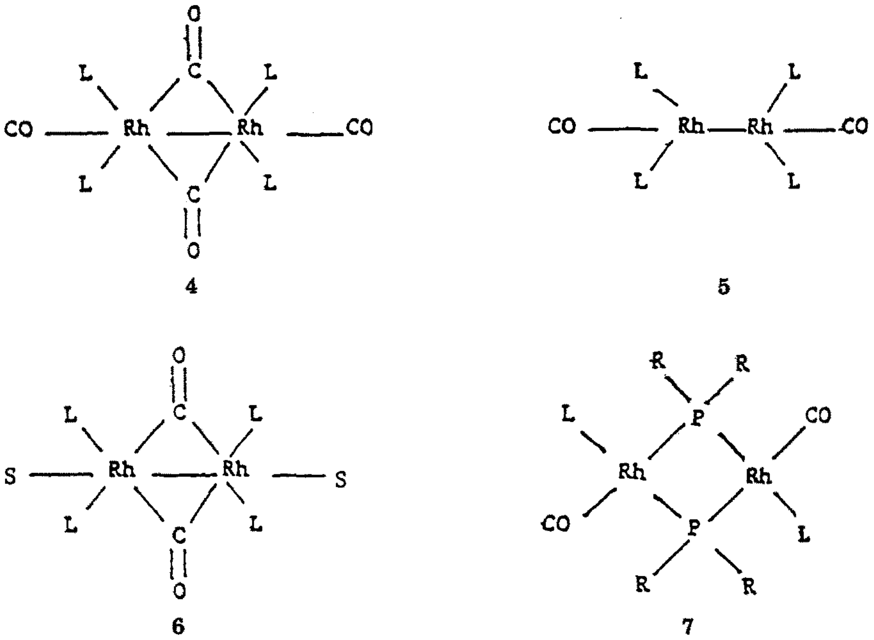


Fig. 2. Room temperature IR spectrum under syngas of triphenylphosphine derivative 1 in dichloroethane.



4 5 6 7

Fig. 3. Dimeric rhodium carbonyl phosphine complexes where L is a triarylphosphine.

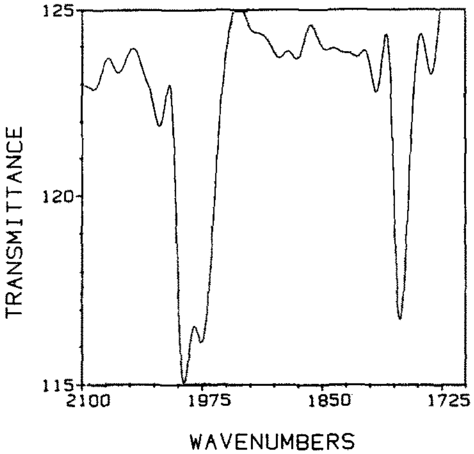


Fig. 4. Room temperature, deconvoluted IR spectrum of the reaction mixture from dodecacarbonyltetrarhodium and triphenylphosphine (1:6) in dichloroethane under nitrogen.

first stage in the catalyst preparation is shown in Fig. 4 when the ligand was triphenylphosphine.

Each of the pre-formed active catalysts shown in Fig. 1 was reacted with 1-hexene after the syngas atmosphere was replaced with nitrogen. These reactions resulted in the facile formation of $RhR(CO)_2L_2$ in solution, in which the metal carbonyl absorption frequencies in the alkyl complexes were slightly shifted as compared to the hydride complexes. When the ligand was triphenylphosphine, the metal carbonyls appeared at 1987 and 1939 cm^{-1}, as shown in Fig. 5. This Figure also shows absorptions for an olefin overtone band at 1819 cm^{-1} and a small amount of the yellow dimer 4, as indicated by a weak band at 1774 cm^{-1}. When the reaction is repressurized with syngas and heated to the hydroformylation temperature of 70 °C, the bands due to the yellow dimer 4 disappear in dichloroethane but not in iso-octane.

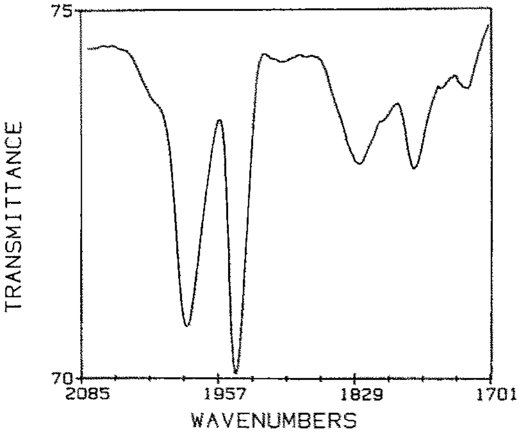


Fig. 5. Room temperature IR spectrum of $Rh(C_6H_{13})(CO)_2L_2$ from reaction of 1 (R_3P = triphenylphosphine) with 1-hexene under nitrogen in dichloroethane.

Our assignment of the 1987 and 1937 cm^{-1} bands to the alkylrhodium complex seems to contradict Wilkinson and co-workers' assertion that such complexes are not stable [13], a conclusion reached on the basis of experiments with ethylene. Since the species clearly contains two terminal carbonyl groups and no hydride, the other reasonable possibility is the acylrhodium complex $Rh(RCO)(CO)_2L_2$. Based on studies of analogous iridium complexes, it would be expected that the alkyl- and acylrhodium complexes would display Rh—CO absorptions of nearly identical frequency [20]. We rejected the acylrhodium structure because of its lack of stability in the absence of a CO atmosphere [20] and because of our failure to detect any carbonyl absorptions for the acyl group for any of the phosphine derivatives (*vide infra*).

To show that the electron density around the catalytically active rhodium center was adjustable in a regular way by modifying the phosphine ligands, Hammett plots were constructed from the IR absorption frequencies for the $RhH(CO)_2L_2$ catalysts 1. The modified Hammett plot (wavenumbers *vs.* sigma constants) for the metal hydride stretching frequency is shown in Fig. 6, and a similar plot for the two metal carbonyl absorptions is illustrated

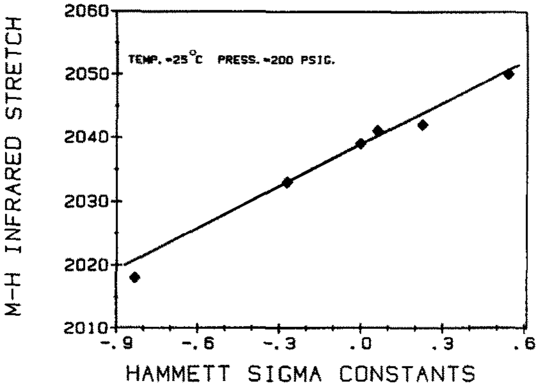


Fig. 6. Hammett plot of the metal hydride stretching frequencies in $RhH(CO)_2L_2$ (1) *vs.* σ in dichloroethane.

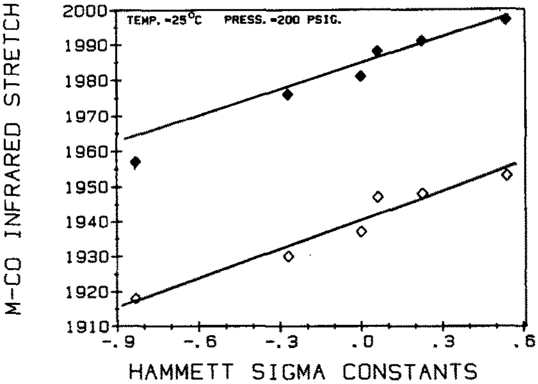


Fig. 7. Hammett plot of the two rhodium carbonyl stretching frequencies in $RhH(CO)_2L_2$ (1) *vs.* σ in dichloroethane.

in Fig. 7. A plot of the two rhodium carbonyl frequencies observed after the reaction of the hydride with excess olefin under nitrogen, affording the metal alkyl species, $Rh(C_6H_{13})(CO)_2L_2$, is illustrated in Fig. 8. These data show that the electron density on the rhodium atom in the hydroformylation system may indeed be adjusted by a proper selection of phosphine coordinating ligands which vary from electron-donating to electron-withdrawing. Since only *para*-substituted arylphosphines were utilized in this study, the hydroformylation rates may now be measured where the steric environment around the active rhodium atom is nearly constant for all of the catalysts. Thus, the effect of gradual electronic adjustment on the active hydroformulation rates was examined to determine whether these rates responded linearly to electronic factors.

Electronic effects on hydroformylation rates

The rates of hydroformylation were measured in both isooctane and dichloroethane using two semi-batch reactors. Rate measurements for

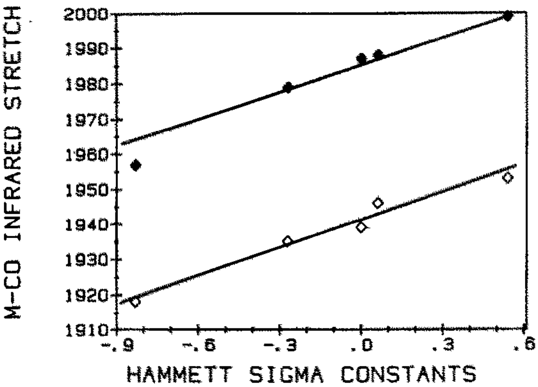


Fig. 8. Hammett plot of the metal carbonyl frequencies in $RhR(CO)_2L_2$ obtained from the reaction under nitrogen of complexes 1 with 1-hexene at 25 °C in dichloroethane.

Hammett correlations were taken using PR_3/Rh ratios of 4:1 in 100 ml magnetically stirred high pressure autoclaves at 70 °C and 200 psi (1.38 MPa) under a 1:1 H_2/CO syngas atmosphere. The catalysts were independently prepared from Rh_2O_3 and phosphine under syngas, as detailed in the experimental section. Rates were sometimes determined by measuring gas absorption up to 30% or less hexene conversion. For very fast reactions this method was preferred. Another method used 30 ml direct drive stirred high pressure CIR autoclaves also operating at 70 °C and 200 psi (1.38 MPa). This method permitted the simultaneous evaluation of the instantaneous concentrations of both 1-hexene and the aldehyde products. The latter experiments used pre-synthesized catalysts 1 from $Rh_4(CO)_{12}$ and PR_3 with PR_3/Rh ratios of 6:1. They were excellent for rate evaluations of all catalysts except those very fast reactions where the 1-hexene was 100% converted within 15 min.

The rate data obtained for the Hammett treatment as a function of phosphine modification of the catalysts are shown in Table 1 for the dichloroethane system.

Since hydroformylation studies reported in the literature were often carried out in hydrocarbon solvents, it was interesting to compare the reactivity in an isooctane solvent to the dichloroethane system. A study of the activity in isooctane using the same substituents and conditions reported in Table 1 showed that the reactivity in dichloroethane was uniformly greater than in isooctane. The triphenylphosphine rate ratio was 4.3 times greater in dichloroethane.

To understand this difference in reactivity, the *in situ* CIR–FTIR spectra were measured for the steady state active systems in both solvents at 70 °C and pressures of 200 psi (1.38 MPa) for DCE and 330 psi (2.28 MPa) for isooctane using the triphenylphosphine system. A typical spectrum in dichloroethane after high conversions of 1-hexene is shown in Fig. 9, which exhibits catalyst bands in the 2000 cm^{-1} region due mainly to $RhH(CO)_2[P(C_6H_5)_3]_2$, along with the aldehyde product band at 1723 cm^{-1} and 1-hexene band at 1637 cm^{-1}. However, the broad-band *in situ* spectrum

TABLE 1

Effect of phosphine substitution on hydroformylation rates and selectivities in dichloroethane

Phosphine substitution	Rate (moles CO/min × 10^4)	Selectivity (linear/branched)
p-N(CH$_3$)$_2$	0.03	2.85
p-OCH$_3$	1.23	3.17
p-H	4.31	3.46
p-F	4.65	3.45
p-Cl	5.62	4.72
p-CF$_3$	6.11	4.95

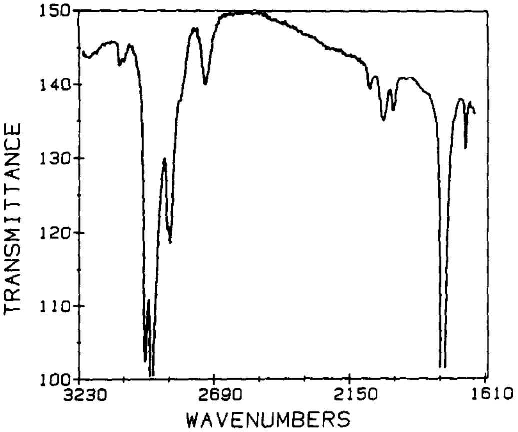


Fig. 9. Broad-band IR spectrum of an active hydroformylation reaction in dichloroethane at 70 °C under 200 psi (1.38 MPa) of syngas using the triphenylphosphine complex 1.

taken for the isooctane reaction at low conversion, shown in Fig. 10, illustrates two interesting phenomena. First, the rhodium carbonyl bands in the 2000 cm^{-1} region do not correspond to RhH(CO)$_2$(PR$_3$)$_2$, but to rhodium dimers; second, their intensity is far too great for solution species. It is typical of the CIR method that the crystallization of solids onto the CIR crystal during reaction leads to abnormally intense absorption bands. Thus, we conclude that the rates of rhodium-catalyzed hydroformylation reactions in nonpolar hydrocarbon media are lower than in dichloroethane due to the presence of sizeable quantities of inactive, insoluble catalysts in the former. When these reactors were opened at the end of the experiment, the isooctane system contained large quantities of insoluble catalysts.

The *in situ* spectrum of the metal carbonyl region after high olefin conversion in isooctane is shown in Fig. 11. This spectrum demonstrates only the presence of the yellow dimer 4, showing bands at 2017, 1987, 1797 and 1772 cm^{-1}. These data also suggest that the interpretation of rate data as a function of PR$_3$/Rh ratios [24] in the prior literature may be clouded due to

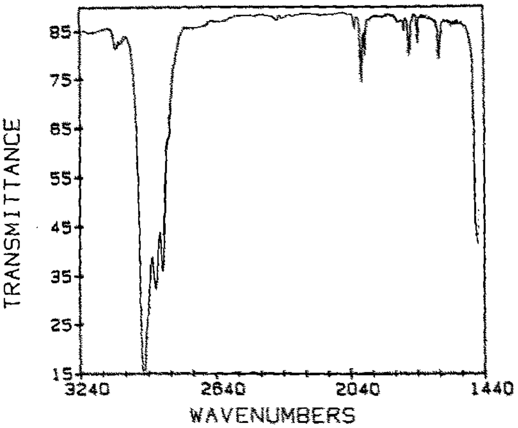


Fig. 10. Broad-band IR spectrum of an active hydroformylation reaction in isooctane at 70 °C under 330 psi (2.28 MPa) of syngas at low olefin conversion using the triphenylphosphine complex 1.

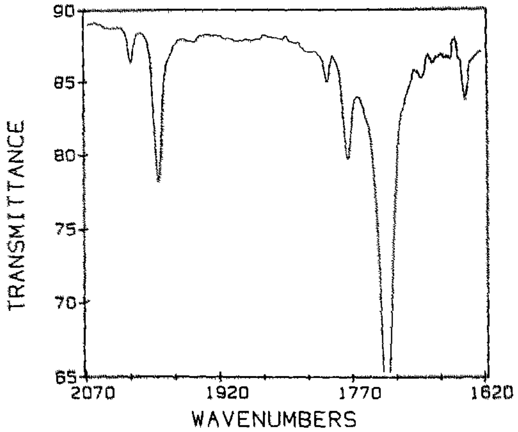


Fig. 11. Partial IR spectrum of an active hydroformylation reaction mixture in isooctane at high conversion (same conditions as in Fig. 10).

the differing degree of catalyst solubilization as a result of the excess phosphine ligand. Furthermore, since most of the process parameter studies reported in the literature were carried out in hydrocarbon solvents, these data may have been substantially influenced by varying amounts of insoluble catalyst.

The Hammett treatment of the data taken in dichloroethane (Table 1) is shown in Fig. 12. The plot appears to be divided into two regions. The electron-withdrawing region from p-H to p-CF_3 ($\sigma = 0.00$ to $+0.54$) shows a nearly linear rate increase by a factor of 1.4. The corresponding rate factor taken from Table 1 for isooctane was 3.2, and this series also gave a similar Hammett plot of rate data *versus* σ constants. The substantially lower rates for the p-OCH_3 and p-$N(CH_3)_2$ reactions were shown, by studies to be

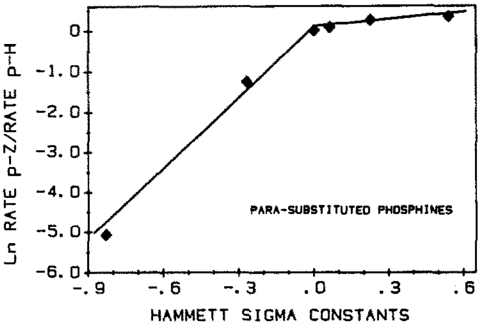


Fig. 12. Hammett plot of relative hydroformylation rates of 1-hexene measured at 70 °C and 200 psi (1.38 MPa) of syngas in dichloroethane. The substituents are those indicated in Fig. 1.

reported separately, to be due to rapid formation of inactive species during the course of the reaction.

The electronic variation studies show that as the electron density on the rhodium atom is reduced by the electron-withdrawing functionality on the modifying phosphine ligand, the rates of reaction increase. In the mechanistic section, the relationship between this observation and the linear increase in the metal carbonyl stretching frequency as the ligand became more electron-withdrawing will be discussed.

Electronic effects on aldehyde selectivities

The selectivities for the formation of linear (2) and branched (3) aldehydes for the rhodium/phosphine-catalyzed hydroformylation of 1-hexene as a function of electronic modification by substituted phosphines are shown in Table 1. These data correlated well in the Hammett treatment shown in Fig. 13 except for the reaction using p-N(CH$_3$)$_2$. It should be noted that these data show that the linear-to-branched aldehyde ratio modestly increased in a linear fashion as the electron density on rhodium decreased. The correlation of the rate and selectivity data by the Hammett treatment follows the same trends reported earlier [21, 22] using rigid diphosphines

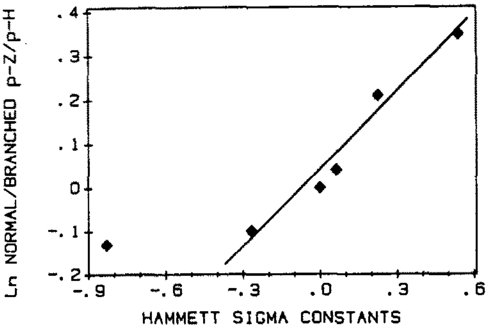


Fig. 13. Hammett plot of the linear-to-branched aldehyde ratio as a function of the p-Z substituent in the phosphine (see Fig. 12).

with substituted monophosphine ligands. The observation that the p-$N(CH_3)_2$ catalyst deviated substantially from the selectivity predicted by the Hammett correlation suggests that the main course of this reaction proceeded by a mechanism different from that of the other derivatives. Indeed, our *in situ* CIR–FTIR studies showed that a bridged phosphido rhodium complex (7) was eventually observed after the reaction temperature of 70 °C was reached, and that the $RhH(CO)_2L_2$ species was formed only in low concentrations under steady state conditions. This reaction was dominated by the orange dimer 5 over a wide range of 1-hexene conversions.

In situ catalytic intermediate studies

The $RhH(CO)_2(PR_3)_2$ catalysts were reacted with a 150-fold excess of 1-hexene in 0.010 M solutions of the rhodium complex in dichloroethane where all species were soluble at the reaction temperature. After pressurization with 200 psi (1.38 MPa) of syngas, the CIR autoclave was rapidly heated to 70 °C. The gas pressure was maintained at 200 psi during the course of the reaction, and the catalytic intermediates were observed by CIR–FTIR as a function of both 1-hexene conversion and reaction time. The *in situ* IR data showed that the corresponding $RhH(CO)_2(PR_3)_2$ complex could be observed to some degree in all of the reactions using the substituted phosphines listed in Fig. 1. However, depending upon the electronic properties of the modifying ligand and the degree of olefin conversion, the relative concentrations of the observable intermediates changed. Figure 14 shows the steady state data for three hydroformylation reactions using the p-H, p-Cl and p-CF_3-substituted phosphines near the 30% olefin conversion stage in each reaction. Figure 14A shows that the predominant intermediate is the metal hydride 1, $RhH(CO)_2L_2$, when the *para* substituent is H. However, as the electron-withdrawing power of the modifying phosphine

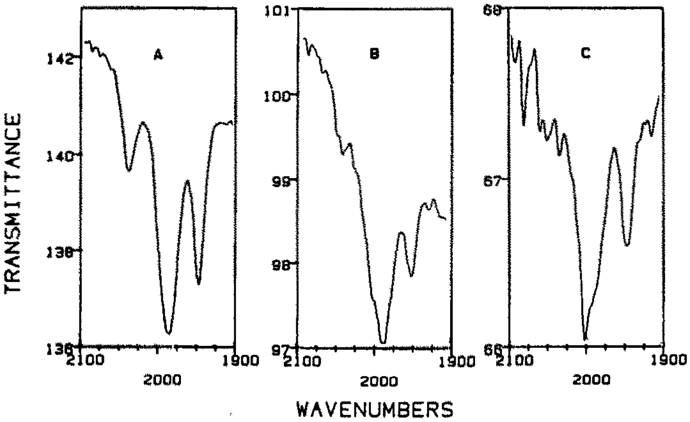


Fig. 14. IR spectra of active hydroformylation reactions after 30% olefin conversion under 200 psi (1.38 MPa) of syngas in dichloroethane at 70 °C for three different phosphines: spectrum A, p-H; spectrum B, p-Cl; spectrum C, p-CF_3.

increases as in *p*-Cl, Fig. 14B, and *p*-CF_3, Fig. 14C, the predominant observable species changed to $Rh(C_6H_{13})(CO)_2L_2$. These species were identified in the latter two cases by a comparison of the spectra to those obtained when their hydrides 1, $RhH(CO)_2(PR_3)_2$, were reacted with an excess of 1-hexene. The data suggest that decreasing the electron density on rhodium by way of *p*-Cl or *p*-CF_3 shifts the rate-limiting step from a point in the catalytic cycle just after formation of $RhH(CO)_2L_2$ (*p*-H) to a point in the cycle just after formation of $RhR(CO)_2L_2$ (*p*-Cl and *p*-CF_3).

The *in situ* spectra for the *p*-H, *p*-Cl and *p*-CF_3 reactions after 98 - 99% 1-hexene conversions are shown in Fig. 15. A comparison of the spectrum in Fig. 15A for the *p*-H reaction at 99% conversion with that in Fig. 14A for 30% conversion shows that the former has undergone only a modest increase in the center band near 1976 cm^{-1}, and the main intermediate was still the dicarbonyl hydride 1. However, the *p*-Cl and *p*-CF_3 spectra shown in Figs. 14B and 14C, respectively, had substantially changed from those of the $RhR(CO)_2L_2$ species, observed at 30% conversion, to mainly single band spectra shown in Figs. 15B and 15C. The metal carbonyl bands at 1981 cm^{-1} for *p*-Cl (Fig. 15B) and 1988 cm^{-1} for *p*-CF_3 (Fig. 15C) correspond, after correction for the substituent wavenumber shift, to the orange dimer 5 which absorbs at room temperature in dichloroethane at 1978 cm^{-1} (*p*-H). On average, the *p*-Cl-substituted metal carbonyls absorb six wavenumbers higher than *p*-H derivatives, as indicated by the spectra for $RhH(CO)_2(PR_3)_2$; *p*-CF_3 derivatives absorb on average 13 wavenumbers higher. In the *p*-CF_3 case, the change in the spectra between the 30% conversion point (Fig. 14C) and the 99% conversion point (Fig. 15C) took place in only 13 minutes; bands for the dicarbonyl hydride 1 reappeared in the spectrum after all of the olefin was converted.

We searched the reaction spectra at various conversions for evidence of appreciable quantities of acylrhodium complexes, which would be expected

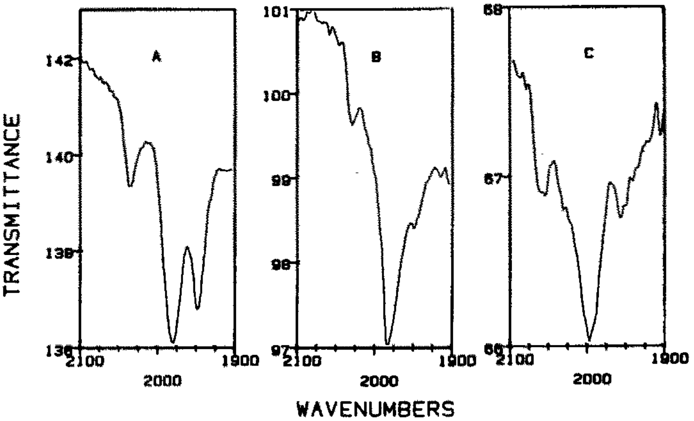


Fig. 15. IR spectra of active hydroformylation reactions after 99% olefin conversion: spectrum A, *p*-H; spectrum B, *p*-Cl; spectrum C, *p*-CF_3.

to show a carbonyl band near 1640 cm^{-1} [20]. The presence of the alkene band at 1637 cm^{-1} obviously complicates the problem. However, since the frequency of the carbonyl band is known to vary with arylphosphine substitution [25], we expected it to be detectable for at least some of the complexes. No significant band attributable to such a species could be found.

Studies at low syngas pressures

To gain more information on the mechanism of hydroformylation, several additional reactions were studied in which aldehyde formation was correlated with IR changes.

Using the standard conditions for the triphenylphosphine (*p*-H) system, a reaction was carried out in dichloroethane under syngas (1:1 CO/H_2) which was diluted by 90% with nitrogen. As the syngas was consumed, the total pressure was maintained at 200 psi (1.38 MPa) by the periodic addition of pure 1:1 CO/H_2. Product analysis for this reaction afforded an interesting comparison with that for the normal reaction carried out in pure 1:1 CO/H_2. These data are shown in Table 2, which includes the results of substituent variation on several reaction variables.

TABLE 2
Percent hydrogenation and isomerization of 1-hexene as a function of reaction variables

Phosphine substitution	Percent hydrogenation	Percent isomerization
p-$N(CH_3)_2$	0.0	0.0
p-OCH_3	1.9	0.3
p-H	1.7	0.4
p-F	2.0	0.5
p-Cl	2.8	1.4
p-CF_3	2.9	1.3
p-H (10% syngas)	16.8	17.2
p-H (PR_3:Rh/90:1)	3.0	1.6

The syngas dilution experiment (10% syngas in Table 2), compared to the pure syngas reaction (*p*-H in Table 2), caused an increase in both hydrogenation (from 1.7% to 16.8%) and in isomerization (from 0.4% to 17.2%), consistent with the data reported by Olivier and Booth [24]. IR spectra from the dilute syngas experiment showed a single band at 1978 cm^{-1} which persisted even after 50% conversion, during which time the rate of olefin conversion was low. The rate increased substantially when the syngas partial pressure was increased. The color of the solution at the end of the dilute syngas reaction was orange. Yagupsky and co-workers [26] reported that the metal carbonyl in the orange dimer 5 absorbed at 1965 cm^{-1} at room temperature in benzene, and that the compound absorbed at 1980 cm^{-1} at room temperature when in equilibrium with the CH_2Cl_2 solvated complex 6. Our *in situ* experiments in DCE solvent showed that the orange dimer band appeared at 1978 cm^{-1}. Thus, we assign the 1978 cm^{-1} band in the dilute syngas experiment to the orange dimer 5. The *in situ* spectra showed no evidence for $RhHL_3$ or $RhHL_4$.

Studies at high PR_3/Rh ratios

Prior literature studies [7, 24] showed that a maximum in rate of hydroformylation and a leveling in selectivity occurred at P/Rh atom ratios of 28 - 30. Reaction rates sharply dropped when studied at atom ratios of 175. This rate decline was usually attributed to the removal of active catalyst from solutions through formation of $RhH(CO)(PR_3)_3$.

A 90:1 P/Rh atom ratio was used in a hydroformylation experiment with 1-hexene at 70 °C and 200 psi (1.38 MPa) of 1:1 syngas in dichloroethane. The reaction described earlier (P/Rh ratio of 6:1) showed that the main species observable to high conversions was $RhH(CO)_2L_2$. The results for the 90:1 reaction showed the same species; however, it was accompanied by the orange dimer 5 (peak at 1978 cm^{-1}) whose concentration increased with time. One hour after 100% conversion of the olefin, the orange dimer 5 was dominant. The spectra clearly showed no evidence for $RhH(CO)(PR_3)_3$, which has generally been thought to be responsible for retarding hydroformylation rates at high P/Rh ratios. The high P/Rh ratio produced only very modest increases in olefin isomerization and hydrogenation (Table 2). High P/Rh ratios increased the linear/branched ratio to 6 from the 3.5 observed under standard conditions (Table 1).

Hydroformylation mechanism

The CIR–FTIR and semi-batch reactor studies reported here, in combination with prior literature data, seem most consistent with the hydroformylation mechanism shown in Fig. 16. The catalytic cycle shown in the Figure is proposed to be the main hydroformylation cycle, where the rate-limiting step when L equals triphenylphosphine is the dissociation of CO from the dicarbonylhydride 8, forming the intermediate carbonylhydride 9. Note that the dicarbonylhydride 8 is drawn directly in the Scheme to emphasize our view that it is an intermediate within the catalytic cycle, rather than a passive species standing outside which only supplies rhodium to it. Our evidence that complex 8 is an active species is that the *in situ* data show that it reacts rapidly with 1-hexene, forming $RhR(CO)_2L_2$; it reformed readily upon exposure of this alkyl complex to syngas at room temperature and above; and it disappeared from the active hydroformylation solutions by forming the metal alkyl 12 when the *para*-substituent on the phosphine became electron-withdrawing (*p*-Cl and *p*-CF_3). Under autogenous conditions it was the dominant species under variable syngas pressures and at four different catalyst concentrations between 0.0025 and 0.0201 M.

The evidence that CO dissociation from 8 is the rate-limiting step, when L equals triphenylphosphine, was the known inverse dependence of reaction rates on CO when 1-hexene is the substrate [23]. The observation that

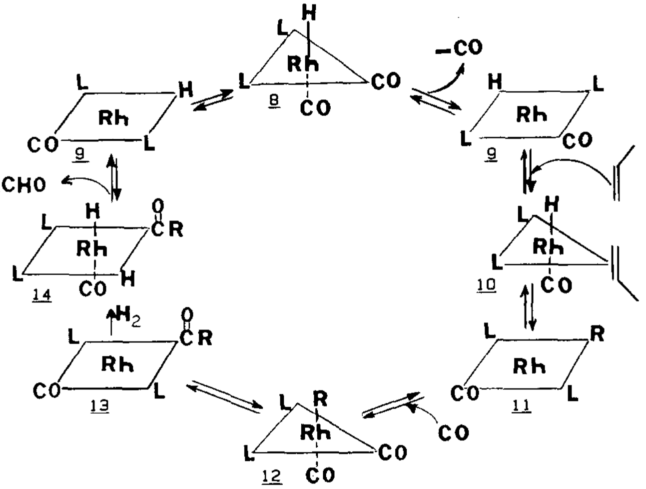


Fig. 16. Principal catalytic cycle of the proposed hydroformylation mechanism.

electron-withdrawing substituents on the ligand linearly increase carbonyl stretching frequencies (Fig. 7) provides evidence that the metal-to-carbonyl bond was also weakened as the increasingly electron-withdrawing ligands reduce M—CO $d\pi$–$p\pi$ interactions. The same electron-withdrawing ligand trend caused hydroformylation rates to increase as shown in Fig. 12. The intermediacy of $RhR(CO)_2L_2$ (12) was established by the observation that all of the $RhH(CO)_2(PR_3)_2$ substituted phosphine derivatives rapidly produced CIR–FTIR-observable solution species of these alkyl complexes when exposed to olefin under nitrogen. When the electron-withdrawing properties of PR_3 were sufficiently high, $RhR(CO)_2(PR_3)_2$ species were the dominant intermediates under autogenous conditions.

A careful examination of the 1600 to 1700 cm^{-1} region of the CIR–FTIR spectra for all of the reactions studied showed no evidence for an acylrhodium species. The olefin stretching frequency under autogenous conditions appeared at 1637 cm^{-1}. This absorption could have interfered with the observation of the acylrhodium; however, one would not expect this coincidental overlapping of the olefin and acyl absorptions for all six of the phosphine-modified systems studied. Since none of the acylrhodium complex could be detected under steady state conditions, the recent suggestion by Collman and co-workers [27] of a bimolecular metal hydride reaction with a metal acyl to form aldehyde directly seems unlikely under our conditions. This point was especially emphasized in the p-CF_3 case, which was fastest, where little $RhH(CO)_2L_2$ and no metal acyl were observed. Since the rate of 1-heptene hydroformylation was also found [23] to demonstrate a first-order H_2 dependence under conditions similar to ours, this suggests that the equilibrium between the alkyl 12 and acyl 13 is far toward 12. The fact that the cycle permits the accumulation of the alkyl intermediate 12 as PR_3 becomes more electron-withdrawing is consistent with a speeding up of the

CO dissociation, 8 to 9, and simultaneous slowing down of the oxidative addition of H_2 to the acyl intermediate 13 to form 14.

The increased rates of hydrogenation and isomerization at low partial pressures of syngas is consistent with the proposed mechanism and with previous observations. A slower rate of conversion of 11 to 12 allows more equilibration between 10 and 11, and thus greater isomerization. Furthermore, under conditions where intermediates 8 - 11 accumulate, the formation of orange dimer 5 is favored, as verified by our observations.

The observation that the selectivity for linear aldehyde increased as the electron-withdrawing properties of PR_3 increased is consistent with the expected shortening of the metal–olefin bond in the complex 10, leading to increased steric control of selectivity in formation of the metal alkyl 11.

The experiments using large P/Rh atom ratios clearly showed that the reduction in the hydroformylation rate was not due to removal of rhodium from the catalyst cycle through $RhH(CO)(PR_3)_3$ formation, as has been generally assumed. The *in situ* spectra showed no evidence of this hydride over the whole range of olefin conversions. Instead, the data showed that the reaction was deactivated through formation of the orange dimer 5. The *in situ* spectra using a P/Rh atom ratio of 90 showed that the principle intermediates under autogenous conditions were $RhH(CO)_2(PR_3)_2$, 1, and the orange dimer 5. The enhancement in linear aldehyde selectivity, commonly observed at high P/Rh ratios [23], may be due to the operation of a rhodium hydroformylation cycle where each intermediate contains three phosphines per rhodium, as suggested by the Celanese studies [21, 22]. To examine this question more fully, three systems were carefully analyzed for the presence of $RhHL_3$, $RhHL_4$ and $RhH(CO)L_3$ where they had the greatest likelihood of forming. The 90/1 PR_3/Rh experiment demonstrated strong IR bands from low to high olefin conversion at 2038, 1982, 1976 and 1939 cm^{-1} (assigned to dimer 5 and hydride 1). There was no evidence for even weak bands near 2020 or 2000 cm^{-1} for $RhHL_3$ and $RhH(CO)L_3$, respectively, in these *in situ* catalytic runs. The syngas dilution experiment afforded a single intense band at 1978 cm^{-1} and no others. An examination of the expanded spectrum for the normal oxo reaction in Fig. 9 showed no evidence for either of the trisliganded species mentioned above. These data do not refute the existence of these species in the active catalytic cycle in extremely low concentrations. However, the data clearly show that under catalytic conditions, if they are present, their steady state concentrations are exceedingly low.

The fact that large changes in the P/Rh ratio produce very minor changes in the percentages of isomerization and hydrogenation products is consistent with our mechanism in which phosphine association and dissociation play no role.

Under the conditions where most of these hydroformylations have been studied, *i.e.* P/Rh of 6:1, the plausibility of the cycle in Fig. 16 is further demonstrated by examining the predominant intermediates at various olefin conversions, for strongly electron-withdrawing phosphines. The spectra for both the *p*-Cl and *p*-CF_3 reactions showed that the $RhH(CO)_2L_2$ catalyst 1 was rapidly converted to $RhR(CO)_2L_2$ upon reaction with olefin under nitrogen. When the reactor was repressurized with syngas and heated to 70 °C at 200 psi (1.37 MPa), the hydride $RhH(CO)_2L_2$ was again detectable up to 5 - 10% olefin conversion. The spectra then changed to show only the alkyl complex $RhR(CO)_2L_2$ up to 60 - 70% olefin conversion. As the olefin concentration further decreased, $RhH(CO)_2L_2$ reappeared until the 99% conversion point, where the principle species was the orange dimer 5. For a mechanistic cycle composed of several elementary reactions of similar rates, the observed alteration in concentration of the observable intermediates upon modest electronic variation is entirely consistent with the cycle in Fig. 16. The formation of the orange dimer 5 at 99% conversion is consistent with Wilkinson's experience [26].

Conclusions

The high pressure CIR–FTIR studies have shown that the principle catalytic cycle in phosphine-modified rhodium hydroformylation is that illustrated in Fig. 16, and is rate limited by CO dissociation from the trigonal bipyramidal catalyst 1. Upon altering the electronic character of the catalyst, other intermediates in the catalytic cycle became observable. The deactivation of the catalytic cycle through formation of the orange dimer 5 was demonstrated. Process conditions which gave rise to high concentrations of this dimer led to low rates, but selectivities were improved due to the conversion of the dimer to catalytic intermediates possibly containing three phosphines per rhodium, as proposed before [28]. This promotes linear aldehyde formation due to the greater steric requirements of this type of catalyst.

It was shown that hydroformylations in hydrocarbon solvents using P/Rh atom ratios of 6:1 led to precipitation of insoluble rhodium complexes in the reactor. These insoluble materials gave greatly reduced rates compared to the soluble catalyst systems formed in dichloroethane.

Experimental

CIR–FTIR experiments

The *in situ* Fourier-transform IR experiments were carried out between 160 psi (1.10 MPa) and 350 psi (2.41 MPa) in a CIR–FTIR high pressure, 316 stainless steel autoclave equipped with a cylindrical internal reflectance crystal obtained from Barnes Analytical. The reactor was equipped with a direct drive stirrer, a high pressure gage, and a thermocouple located in the reaction medium. The optical bench used was the standard CIRCLE* equipment. The reactors had an internal volume adjustable to 30 ml and were equipped with either a silicon or zinc selenide CIR crystal.

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*The optical bench is a CIRCLE accessory obtained from Barnes Analytical. Its configuration as used for these CIR–FTIR analyses was described in [15].

A typical reaction procedure involved loading the autoclave with the tetrarhodium dodecacarbonyl, phosphine and purified dried solvent in a dry box. The autoclave was sealed, removed from the dry box, and placed on the optical bench where the heating elements were put into place and the CIR crystal aligned. The experiments usually required the prior preparation of the $RhH(CO)_2(PR_3)_2$ catalysts, which required first stirring the reaction mixture at room temperature under nitrogen for nearly an hour while IR spectra were obtained. Then the reactor was pressurized with a 1:1 H_2/CO mixture at 160 psi (1.10 MPa) at room temperature, usually for 1 h, while the IR spectra were monitored. The reactor was removed from the FTIR and placed in the dry box where it was opened. After 1-hexene was added, the autoclave was immediately resealed and repositioned on the optical bench. The development of the alkyl complexes, $RhR(CO)_2(PR_3)_2$, was monitored; they were usually fully formed by the time the first spectra could be recorded, about 5 min. The reactor was repressurized with 200 psi (1.38 MPa) of 1:1 H_2/CO and rapidly heated to 70 °C. IR spectra were measured during the heat-up time and after the desired reaction temperature was reached. Using the integration facilities on the Nicolet 60SX FTIR spectrometer*, the concentrations of the rhodium carbonyl intermediates, of 1-hexene and of both aldehydes were followed with time. The solutions were initially 0.010 M in Rh, 0.060 M in phosphine, and 1.372 M in 1-hexene, unless otherwise noted.

Catalyst preparation

First stage

All of the *para*-substituted triarylphosphine ligands were reacted with tetrarhodiumdodecacarbonyl in dichloroethane at room temperature under nitrogen, and the course of their synthesis was followed by CIR–FTIR. All of the reaction mixtures showed IR spectra consistent with the presence of complexes previously identified by Wilkinson and co-workers [12, 26]. In the case of the triphenylphosphine derivative, the principal species in solution was the yellow dimer 4, giving bands at 2022, 1995, 1793 and 1771 cm^{-1}. A moderate-sized absorption at 1978 cm^{-1} arose from the orange dimer 5, and a small concentration of the red dimer 6 gave a band at 1740 cm^{-1}. Curve resolution techniques were not adequate to permit reliable measurements of the concentrations of these species due to overlapping peaks.

Second stage

The nitrogen in the above reaction was replaced by 160 psi (1.10 MPa) of syngas and the mixture was stirred. All of the substituted phosphines formed the trigonal bipyramidal complexes, $RhH(CO)_2(PR_3)_2$; their hydride and carbonyl stretching frequencies are recorded in Table 1. All were contaminated with small amounts of the yellow dimer, even after reaction times of 2 h.

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*The Nicolet 60SX FTIR was equipped with an MCTB detector.

Third stage

The reactors containing the carbonyl hydride complexes were placed in the dry box where 1-hexene was added and the autoclave rapidly re-sealed and purged with nitrogen. After about 5 min the IR spectra could be measured; those which showed exceptionally clean peaks for the alkyl complexes, $Rh(C_6H_{13})(CO)_2(PR_3)_2$, are reported here: *p*-methoxy, 1979, 1935 cm^{-1}; *p*-hydrogen, 1987, 1935 cm^{-1}; *p*-trifluoromethyl, 1997, 1953 cm^{-1}.

Autogenous reactions

The alkyl complexes were treated with 200 psi (1.38 MPa) of syngas at room temperature and the reactors immediately heated to 70 °C, where they were maintained throughout the reaction. The reaction was usually monitored for 2 or more h depending on the rate of the reaction; the concentrations of the olefin and aldehydes were determined from the stored spectra. At the end of the reaction, the reactor was cooled and its contents analyzed by GLC to determine product selectivities as well as to check total aldehyde yields.

Spectra collection

Infrared spectra were usually collected at a spectral resolution of 4 cm^{-1} using 200 to 2000 averaged spectra. An optimum procedure for obtaining high quality spectra was to measure all background and solvent spectra at 70 °C for subtraction from the active hydroformylation mixtures, and at room temperature for the catalyst syntheses studies. The spectra plotted in the Figures used no smoothing function unless otherwise specified.

Kinetic data

Kinetic experiments were analyzed between 10 and 30% conversion by measuring the total gas absorption as a function of time at 70 °C. These experiments used 100 ml stainless steel, magnetically driven high pressure autoclaves. Using either dichloroethane or isooctane solvent, the reactors were filled in a nitrogen-flushed glove box with Rh_2O_3 and the appropriate phosphine. The rhodium concentration in the final solution was 0.0040 M and a 4:1 molar ratio of phosphine to rhodium was used. The solvent (24.4 g) was mixed with 1.88 g of benzene, which served as an internal standard for the final GLC analysis of the products. After the reagents were mixed, the autoclave was sealed in the glove box, transferred to the high pressure facility and flushed with nitrogen at high pressure several times before being tested for pressure leaks. The reactor was pressurized to 200 psi with syngas, the pressure being released before each subsequent repressurization. The catalyst was then formed by heating the pressurized reactor to 50 °C for 1 h. The autoclave was next cooled to ambient temperature and depressurized as quickly as possible. Then 6.73 g (0.080 mol) of 1-hexene was injected into the autoclave, which was then repressurized with syngas and flushed several times. The autoclave was placed into a thermostatted furnace held at 70 °C. The reactor usually took about 10 min to reach reaction temperature, after which gas absorption data were taken at 5 to 10 min intervals. The pressure was maintained nearly constant at 200 psi (1.38 MPa) by the addition of fresh syngas as needed. The reactions were monitored for 60 min before they were rapidly cooled to room temperature. The reactor was opened and the contents transferred to vials for subsequent GLC analysis, conducted on a 9 ft X 1/8 in stainless steel column packed with 10% OV-101 on silanized Chromosorb W. Isomerization as well as aldehyde yields were measured as a check on the gas absorption data. The reaction rates were evaluated from the slope of the flat portion of the gas absorption curve between 10 and 30% olefin conversion.

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