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Hydroformylation with a Rhodium/Bulky Phosphite Modified Catalyst. Catalyst Comparison for Oct-1-ene, Cyclohexene, and Styrene

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The rhodium-catalyzed hydroformylation of oct-1-ene, cyclohexene, and styrene has been studied using $\text{Rh}(\text{CO})_2\text{Acac}$ as the catalyst precursor and tris(2-*tert*-butyl-4-methylphenyl) phosphite as the ligand ($T = 40\text{--}100\text{ }^\circ\text{C}$, $P_{\text{CO}} = 2.5\text{--}44\text{ bar}$, $P_{\text{H}_2} = 2.5\text{--}50\text{ bar}$, toluene as a solvent). For oct-1-ene, very high hydroformylation rates are obtained ($39.8 \times 10^3\text{ mol}[\text{mol Rh}]^{-1}\text{ h}^{-1}$) under mild conditions ($P_{\text{CO}} = 10\text{ bar}$, $P_{\text{H}_2} = 10\text{ bar}$, $T = 80\text{ }^\circ\text{C}$). The concentration dependencies of the reaction rate show that the rate-determining step is the reaction of H_2 with the acylrhodium complex. A negative order in the CO concentration is observed. For cyclohexene, the reaction rate is lower under the same conditions ($512\text{ mol}[\text{mol Rh}]^{-1}\text{ h}^{-1}$, $[\text{cyclohexene}] = 0.91\text{ M}$), the addition of cyclohexene to the starting rhodium hydride complex now being rate-limiting. In the hydroformylation of styrene, the rate is 3 times lower than that of oct-1-ene. For the formation of the linear 3-phenylpropanal, the rate-determining step is the reaction of H_2 with the rhodium acyl species. CO inhibits the reaction. In contrast with the formation of the secondary 2-octyl species from oct-1-ene, the formation of the secondary (1-phenylethyl)rhodium species is reversible. For the formation of the branched aldehyde, the kinetics depend strongly on the CO partial pressure. At low CO pressures, addition of CO to the proposed (η^3 -1-phenylethyl)rhodium intermediate is slow. At higher CO pressures, hydrogenolysis of the rhodium acyl intermediate is the rate-determining step and the rate decreases with increasing CO.

Introduction

Much research has been conducted to elucidate the mechanism and the kinetics of the rhodium-catalyzed hydroformylation reaction.¹ It is commonly recognized that the reaction mechanism for the cobalt-catalyzed hydroformylation as pointed out by Heck and Breslow² is suitable for the rhodium analogue as well. Markó and co-workers³ and more recently Garland⁴ studied the unmodified rhodium carbonyl catalyst system very extensively. The active species is generally assumed to be $\text{HRh}(\text{CO})_3$, which is formed by dissociation of a CO ligand from the $\text{HRh}(\text{CO})_4$ complex as Vidal and Walker⁵ have evidenced. Very recently Garland⁶ identified $\text{RC}(\text{O})\text{Rh}(\text{CO})_4$ as the only observable reaction intermediate, using high-pressure infrared spectroscopy during the rhodium-catalyzed hydroformylation of 3,3-dimethylbut-1-ene starting with $\text{Rh}_4(\text{CO})_{12}$.

Markó found different kinetic equations for different types of alkenes.³ Using hept-1-ene, under the typical reaction conditions of $P_{\text{H}_2} = 33\text{--}126\text{ bar}$, $P_{\text{CO}} = 40\text{--}170\text{ bar}$, $T = 75\text{ }^\circ\text{C}$, the kinetic expression is the following:

$$\frac{d[\text{aldehyde}]}{dt} = \frac{k[\text{Rh}][\text{H}_2]}{[\text{CO}]} \quad (1)$$

Scheme 1. Generally Accepted Mechanism for the Hydroformylation Reaction Catalyzed by the Unmodified Rhodium Carbonyl Complex

This corresponds with the reaction of H_2 and the rhodium acyl intermediate (Scheme 1, step 6) as rate-determining. Thus as these high pressures, the reaction is inhibited by CO. At lower CO pressures ($P_{\text{CO}} \leq 20\text{ bar}$), the reaction is first order in $[\text{CO}]$, the coordination of CO to the rhodium-alkyl complex (Scheme 1, step 4) now appearing as rate-limiting. This proposal is contradicted⁶ by the observation of $\text{RC}(\text{O})\text{Rh}(\text{CO})_4$ as the only species present in the reaction mixture at 20 bars of pressure. However, the substrate used, 3,3-dimethylbut-1-ene, is a highly substituted alkene and the conditions are not quite the same. This can influence the reaction kinetics rigorously as has been shown recently.⁷ For an internal olefin like cyclohexene and $\text{Rh}_4(\text{CO})_{12}$ as the catalyst precursor, the rate expression

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reported by Markó³ is

$$\frac{d[\text{aldehyde}]}{d[t]} = k[\text{cyclohexene}][\text{Rh}]^{0.25}[\text{H}_2]^{0.5} \quad (2)$$

From the kinetic equation and infrared data,³ it was concluded that the addition of cyclohexene to the hydrido rhodium carbonyl complex is rate-determining with rhodium predominantly in the tetranuclear cluster.

The phosphine- or phosphite-modified catalyst system behaves differently. Several active species may be present in this catalytic system, and the complex that shows the highest linearity is generally accepted to be $\text{HRh}(\text{CO})_2\text{L}_2$, in which L represents an arylphosphine or a small phosphite.⁸ Much research on the kinetics has been conducted, but only Cavalieri d'Oro and his co-workers have studied the catalysis under actual process conditions ($P = 10\text{--}50$ bar, $T = 80\text{--}120$ °C).⁹ Their results (using propene as substrate and triphenylphosphine as ligand) showed that the reaction was zeroth order in both CO and H_2 concentrations, which excludes the hydrogenolysis (Scheme 1, step 6) as being rate-determining. Despite these data, many authors still consider the hydrogenolysis as the turnover-limiting step.

Several reports^{10–12} have appeared using phosphites as auxiliary ligands. These ligands are considered too sensitive to hydrolysis and alcoholysis.¹³ However, phosphites are less sensitive toward oxidation than phosphines and they show, besides lower σ -donor capacities, better π -acceptor properties. The latter feature should make them interesting as modifying ligands covering a wide range of electronic variation. Since the early 1980s, the use of bulky phosphites in the rhodium-catalyzed hydroformylation has been a field of interest.^{11d,f,12a} These ligands show a high reactivity in the hydroformylation of otherwise unreactive olefins¹² and are commercially applied for the formation of 3-methylpentane-1,5-diol.^{12c} In contrast to the assertion that bulky phosphite containing catalysts are not applicable in the hydroformylation of alk-1-enes, we showed earlier a very high reaction rate of the hydroformylation of oct-1-ene using tris(2-*tert*-butyl-4-methyl-

Table 1. Influence of the Phosphite/Rhodium Ratio on the Different Reaction Parameters (Conditions: $T = 80$ °C, $P_{\text{CO}} = P_{\text{H}_2} = 10$ bar, $[\text{Rh}(\text{CO})_2\text{Acac}] = 0.1$ mmol dm^{-3} , $[\text{oct-1-ene}] = 0.86$ mol dm^{-3} in 20 mL of toluene)

run	P/Rh	convn (%)	$k_{\text{ald}} (\times 10^3 \text{ mol mol}^{-1} \text{ h}^{-1})$	n/iso	isom (%)
1	10	31	39.7	2.0	16
2	50	23	38.4	1.9	12
3	50	32	42.5	1.9	12
4	50	30	38.5	1.9	14
5	250	29	43.2	1.9	12

phenyl) phosphite,¹⁴ combined with an average regioselectivity (linear aldehyde:branched aldehyde = 2:1) and a low isomerization rate. A preliminary mechanistic study of this catalytic system was carried out by Jongsma¹⁵ using less reactive cycloalkenes as the substrates. Under 20 bar H_2/CO , the main rhodium species is $\text{HRh}(\text{CO})_3\text{P}$ (P = tris(2-*tert*-butylphenyl) phosphite) as was evidenced by NMR and IR spectroscopy, meaning that only one CO ligand is replaced by the bulky phosphite instead of two, which is the case with triphenylphosphine. Under hydroformylation conditions (after adding alkene), *in situ* IR showed that the same species was most abundant. Thus, his results indicate that the bulky phosphite modified system behaves differently from the triphenylphosphine-modified system.

In this article, we report on the kinetics of the bulky phosphite, tris(2-*tert*-butyl-4-methylphenyl) phosphite, modified system and the mechanism of the hydroformylation reaction is discussed. We studied the effects of H_2 and CO pressures in the hydroformylation of oct-1-ene, cyclohexene, and styrene as well as the influence of the rhodium, ligand, and substrate concentrations.

Results

For all substrates a 100% conversion could eventually be reached. To compare the results properly, we decided to present in the tables data obtained at similar substrate conversions.

Oct-1-ene. First, it was determined which tris(2-*tert*-butyl-4-methylphenyl) phosphite/rhodium ratio was sufficient to be certain that all rhodium particles are converted *in situ* into the active complexes and all the effects measured could be ascribed to the other varied conditions.⁵ Jongsma¹⁵ found an enhancement in reaction rate at increasing phosphite/rhodium ratio and proved that at low phosphite concentrations $\text{Rh}(\text{CO})_2\text{Acac}$ is not converted completely to a hydride. Table 1 summarizes the results of varying the P/Rh ratio. All results remained equal as the P/Rh ratio increased, and it was decided to use a minimum ratio of 50 in the kinetic experiments at a total rhodium concentration of 0.1 mmol dm^{-3} .

An increase of the reaction temperature causes an enhancement of both the rate of hydroformylation and that of isomerization, as can be seen in Table 2. Also a slight increase of the n/iso (n/i) ratio is observable. The zeroth-order reaction rate constant for the formation of aldehyde changes from 1.7×10^3 [mol] [mol Rh]⁻¹ h⁻¹ at 50 °C to 87.3×10^3 [mol] [mol Rh]⁻¹ h⁻¹ at 90 °C,

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Table 2. Temperature Effect on the Hydroformylation Results (Conditions: $p_{\text{CO}} = p_{\text{H}_2} = 10$ bar, $[\text{Rh}(\text{CO})_2\text{Acac}] = 0.1 \text{ mmol dm}^{-3}$, $P/\text{Rh} = 50$, $[\text{oct-1-ene}] = 0.86 \text{ mol dm}^{-3}$ in 20 mL of Toluene)

run	T ($^{\circ}\text{C}$)	convn (%)	$k_{\text{ald}} (\times 10^3 \text{ mol mol}^{-1} \text{ h}^{-1})$	n/iso	isom (%)
6	50	18	1.7	1.5	3
7	60	23	5.3	1.6	4
8	70	38	16.9	1.7	7
2-4 ^a	80	28	39.8	1.9	13
9	90	38	87.3	2.1	24

^a The average values of runs 2, 3, and 4 are given, $\sigma(n-1)(\text{TOF}) = 2.54 \times 10^3$.

Table 3. Substrate Dependency of the Hydroformylation Reaction Rate and Reaction Products (Conditions: $T = 80$ $^{\circ}\text{C}$, $p_{\text{CO}} = p_{\text{H}_2} = 10$ bar, $P/\text{Rh} = 50$, $[\text{Rh}(\text{CO})_2\text{Acac}] = 0.1 \text{ mmol dm}^{-3}$, $P/\text{Rh} = 50$, $[\text{oct-1-ene}] = 0.86 \text{ mol dm}^{-3}$ in 20 mL of Toluene)

run	[oct-1-ene] (M)	convn (%)	$k_{\text{ald}} (\times 10^3 \text{ mol mol}^{-1} \text{ h}^{-1})$	n/iso	isom (%)
10	0.46	44	28.5	1.9	14
11	1.21	24	29.6	1.8	14
12	0.86	43	32.1	1.9	13
13 ^a	1.73	13	46.2	1.7	1.1
14 ^a	0.86	23	43.1	1.7	2.1
15 ^a	0.43	11	30.3	1.7	0.6
15 ^a	0.43	17	24.6	1.7	0.4
15 ^a	0.43	41	23.0	1.7	1.2

^a $p_{\text{CO}} = p_{\text{H}_2} = 40$ bar.

Figure 1. Course of a typical hydroformylation experiment: (▲) percentage of oct-1-ene in the reaction mixture, (□) percentage of formed aldehydes. Conditions: $T = 80$ $^{\circ}\text{C}$, $p_{\text{CO}} = p_{\text{H}_2} = 10$ bar, $[\text{Rh}(\text{CO})_2\text{Acac}] = 0.5 \text{ mmol dm}^{-3}$, $[(2-t\text{-Bu-4-MeC}_6\text{H}_4\text{O})_3\text{P}] = 5 \text{ mmol dm}^{-3}$, $[\text{oct-1-ene}] = 0.86 \text{ mol dm}^{-3}$ in 20 mL of toluene.

and the amount of isomerization products is enlarged from 3% to 24%.

As can be concluded from Table 3 and Figure 1, in our dilute solution, the reaction rate is independent of the octene concentration up to at least 30% conversion. This concentration corresponds to a conversion of 95% if the reaction were carried out in pure octene. In Figure 1, the course of a typical reaction, performed at standard conditions, is drawn and it shows that the octene concentration decreases linearly with the reaction time up to even 60% conversion in this dilute solution. The ratio of the products that are formed (both of the aldehydes and internal octenes) is constant during that time. When the reaction of oct-1-ene begins to slow down, the internal octenes, formed via isomerization of oct-1-ene, are hydroformylated as well, resulting in

Figure 2. Dependency of the reaction rate on the concentration of the catalyst precursor (runs 16–29). ▲ = turnover number. Conditions: $T = 60$ $^{\circ}\text{C}$, $p_{\text{H}_2} = p_{\text{CO}} = 10$ bar, $[(2-t\text{-Bu-4-MeC}_6\text{H}_4\text{O})_3\text{P}] = 5 \text{ mmol dm}^{-3}$, $[\text{oct-1-ene}] = 0.86 \text{ mol dm}^{-3}$ in 20 mL of toluene.

several branched aldehydes and hence causing a disturbance in the initial normal to branched ratios.

We repeated these reactions under pseudo-zeroth-order conditions in CO and H_2 , i.e. 80 bar CO/H_2 (runs 13–15), and these results confirmed what we stated before: in the higher concentration region, no substrate dependency was observed. From $\approx 50\%$ conversion of our standard oct-1-ene concentration ($= 0.86 \text{ M}$), the octene appears in the reaction equation as we found indeed for the low concentration experiment a lower initial rate in agreement with Figure 1. The order we determined for that region was around 0.3.

We also studied the effects of the rhodium precursor concentration on the rate of the hydroformylation reaction. To avoid exothermic temperature effects at high catalyst concentrations and 80 $^{\circ}\text{C}$, we did the measurements at 60 $^{\circ}\text{C}$ and we varied the rhodium concentration from 0.2 to 8 times our standard concentration. From Figure 2 it is clear that the rate of formation of the product aldehydes is linearly proportional to the rhodium precursor concentration. So it can be concluded that the reaction rate has in this low concentration region a first-order dependency on the rhodium concentration. From this figure, it can also be concluded that diffusion of the gases into the solution is not rate-limiting. Otherwise, at enhanced rhodium concentrations, i.e. at higher overall gas consumptions, this diffusion limitation would have shown up in decreased reaction rates, higher amounts of isomerized alkene, and a higher normal (n) to iso ratio. None of these phenomena were observed (see also Experimental Section).

Variation of the total pressure ($p_{\text{CO}}/p_{\text{H}_2} = 1$) causes a slight increase in the hydroformylation reaction rate, and the normal to iso ratio decreases from 2.1 to 1.8 (Table 4). However, the formation of internal octenes, caused by isomerization of oct-1-ene, decreases significantly at higher overall pressures. The table shows that the rate of formation of both the normal and the branched aldehydes as well as the rate of the isomerization reaction is first order in H_2 concentration. No significant change in the n/iso ratio is observable. The hydroformylation reaction rate, however, shows an inverse dependency on the CO partial pressure. At very low CO pressures, the reaction even has a runaway

Table 4. Effect of Variation of Pressures on the Hydroformylation of Oct-1-ene (Conditions: $P/Rh = 50$, $T = 80\text{ }^{\circ}\text{C}$, $[\text{Rh}(\text{CO})_2\text{Acac}] = 0.1\text{ mmol dm}^{-3}$, $[\text{oct-1-ene}] = 0.86\text{ mol dm}^{-3}$ in 20 mL of toluene)

run	P_{H_2} (bar)	P_{CO} (bar)	convn (%)	$k_{\text{ald}} (\times 10^3 \text{ mol mol}^{-1} \text{ h}^{-1})$	n/iso	isom (%)
30	2.5	2.5	28	30.5	2.1	28
4	10	10	30	38.5	1.9	14
31	15	15	28	43.7	1.8	9
32	20	20	32	45.4	1.8	6
4	10	10	30	38.5	1.9	12
33	10	21	28	25.6	1.7	8
34	10	32	30	14.3	1.7	6
35	10	40	17	7.6	1.7	3
8	10 ^a	10	38	16.9	1.7	7
36	20 ^a	10	28	34.9	1.7	6
37	30 ^a	10	28	39.4	1.7	5
38	30 ^a	10	28	42.3	1.7	5
39	40 ^a	10	32	72.4	1.7	5
40	50 ^a	10	28	85.2	1.7	5

^a $T = 70\text{ }^{\circ}\text{C}$.

Figure 3. In plot of the average turnover frequency of the hydroformylation of cyclohexene (calculated by means of the pressure drop) against the reaction time. Δ = turnover number. Conditions: $T = 80\text{ }^{\circ}\text{C}$, $P_{\text{CO}} = P_{\text{H}_2} = 10\text{ bar}$ $P/Rh = 10$, $[\text{Rh}(\text{CO})_2\text{Acac}] = 1\text{ mmol dm}^{-3}$ $[\text{cyclohexene}] = 0.91\text{ mol dm}^{-3}$ in 20 mL of toluene.

character. The CO present in the reaction mixture is consumed so fast that diffusion of CO from the vapor into the solution becomes rate-determining. At increasing CO pressure, the isomerization reaction is suppressed.

Cyclohexene. The hydroformylation of substituted alkenes is, as known, much slower than the hydroformylation of 1-alkenes. For cyclohexene, the ln plot (Figure 3) of conversion vs time shows clearly that the reaction rate is first order in cyclohexene concentration. The rate constant determined from the ln plot is $512\text{ [mol] [mol Rh]}^{-1} \text{ h}^{-1}$ ($T = 80\text{ }^{\circ}\text{C}$, $P_{\text{CO}} = P_{\text{H}_2} = 10\text{ bar}$, initial cyclohexene concentration = 0.91 M), being 80 times lower than for oct-1-ene (note: this comparison is of limited value because the hydroformylation of oct-1-ene shows a zeroth-order dependency in substrate concentration).

In Table 5, the influence of the reaction temperature on the reaction rate is presented. Raising the initial temperature results in an increase of the rate constant. Going from 70 to $100\text{ }^{\circ}\text{C}$, the reaction proceeds faster by a factor of approximately 10. The determined initial turnover frequencies are respectively 176 and 1636 $[\text{mol}] [\text{mol Rh}]^{-1} \text{ h}^{-1}$ ($P_{\text{CO}} = P_{\text{H}_2} = 10\text{ bar}$, initial cyclohexene concentration = 0.91 M).

Table 5. Influence of the Temperature on the Rate of Hydroformylation of Cyclohexene (Conditions: $P_{\text{CO}} = P_{\text{H}_2} = 10\text{ bar}$, $P/Rh = 10$, $[\text{Rh}(\text{CO})_2\text{Acac}] = 1\text{ mmol dm}^{-3}$, $[\text{cyclohexene}] = 0.91\text{ mol dm}^{-3}$ in 20 mL of Toluene)

run	$T\text{ (}^{\circ}\text{C)}$	convn (%)	$k_{\text{ald}} (\text{mol mol}^{-1} \text{ h}^{-1})$
41	70	27	176
42	80	34	512
43	90	37	788
44	100	41	1636

Table 6. CO - and H_2 -Pressure Influence on the Rate of Hydroformylation of Cyclohexene (Conditions: $T = 80\text{ }^{\circ}\text{C}$, $P/Rh = 10$, $[\text{Rh}(\text{CO})_2\text{Acac}] = 1\text{ mmol dm}^{-3}$, $[\text{cyclohexene}] = 0.91\text{ mol dm}^{-3}$ in 20 mL of Toluene)

run	P_{H_2} (bar)	P_{CO} (bar)	$k_{\text{ald}} (\text{mol mol}^{-1} \text{ h}^{-1})$
45	10	10	512
46	15	10	555
47	20	10	573
48	30	10	652
49	10	5	607
50	10	20	324
51	10	30	244
52	10	40	219

Table 7. P/Rh Dependency of Hydroformylation of Styrene (Conditions: $T = 80\text{ }^{\circ}\text{C}$, $P_{\text{CO}} = P_{\text{H}_2} = 11\text{ bar}$, $[\text{Rh}(\text{CO})_2\text{Acac}] = 0.25\text{ mmol dm}^{-3}$, $[\text{styrene}] = 0.89\text{ mol dm}^{-3}$ in 20 mL of Toluene)

run	P/Rh	convn (%)	$k_{\text{ald}} (\times 10^3 \text{ mol mol}^{-1} \text{ h}^{-1})$	iso/n
53	5	21	4.1	3.3
54	20	25	19.8	3.0
55	20	21	14.6	3.4
56	20	19	15.0	3.4
57 ^a	50	19	16.0	3.7
58	200	25	19.6	3.1

^a $[\text{Rh}(\text{CO})_2\text{Acac}] = 0.002\text{ mmol}$ in 20 mL.

Table 8. Influence of the Initial Styrene Concentration on the Reaction Rate and Selectivity (Conditions: $T = 70\text{ }^{\circ}\text{C}$, $P_{\text{CO}} = P_{\text{H}_2} = 11\text{ bar}$, $[\text{Rh}(\text{CO})_2\text{Acac}] = 0.25\text{ mmol dm}^{-3}$, $P/Rh = 20$ in 20 mL of Toluene)

run	$[\text{styrene}] (\text{M})$	convn (%)	iso/n	$k_{\text{ald}} (\times 10^3 \text{ mol mol}^{-1} \text{ h}^{-1})$
59	0.47	38	5.1	11.3
60	0.89	23	5.9	12.0
61	1.27	24	5.5	10.9

The pressure dependencies are clear; the H_2 concentration has a slightly positive effect on the reaction rate (see Table 6), the order in p_{H_2} being approximately 0.2. The CO pressure affects the reaction rate very significantly. The k_0 is decreased by a factor of 3, going from 5 to 40 bar of CO, which corresponds with a negative order in CO (≈ -0.65).

Styrene. From Table 7 it is clear that a P/Rh ratio of 5 is too small to transform all rhodium into an active catalyst but that a ratio of 20 is sufficient.

Variation of the initial styrene concentration hardly influenced the reaction rate and the normal to branched ratio (Table 8). We found an average overall reaction rate of $10.2 \times 10^3\text{ [mol] [mol Rh]}^{-1} \text{ h}^{-1}$ ($T = 70\text{ }^{\circ}\text{C}$, $[\text{styrene}] = 0.89\text{ M}$, rate averaged over about 30% conversion of styrene) which is a factor of 3 lower than the rate found for oct-1-ene.

As in the hydroformylation of other substrates, an increase in temperature leads to an enlarged overall reaction rate but, more noteworthy, to a considerable decrease of the selectivity toward the branched aldehyde

Table 9. Influence of the Reaction Temperature on the Rate and Selectivity of the Hydroformylation of Styrene (Conditions: $P_{\text{CO}} = P_{\text{H}_2} = 11$ bar, $[\text{Rh}(\text{CO})_2\text{Acac}] = 0.25$ mmol dm⁻³, $[\text{styrene}] = 0.89$ mol dm⁻³, $P/\text{Rh} = 20$ in 20 mL of Toluene)

run	T (°C)	convn (%)	iso/ n	$k_{n\text{-ald}}$ ($\times 10^3$ mol mol ⁻¹ h ⁻¹)	k_{isoald} ($\times 10^3$ mol mol ⁻¹ h ⁻¹)
62	51	23	10.6	0.2	2.1
63	60	22	7.6	0.8	5.8
64	70	23	5.9	1.8	10.2
54–56 ^a	80	22	3.3	3.9	12.6
65	90	27	2.1	6.2	12.6

^a Average of runs 54, 55, 56 is given, $\sigma(n-1)(\text{TOF}) = 2.00 \times 10^3$.

Table 10. P_{H_2} and P_{CO} Influence on the Rate and Selectivity of the Hydroformylation of Styrene (Conditions: $T = 80$ °C, $[\text{Rh}(\text{CO})_2\text{Acac}] = 0.25$ mmol dm⁻³, $P/\text{Rh} = 20$, $[\text{styrene}] = 0.89$ mol dm⁻³ in 20 mL of Toluene)

run	P_{H_2} (bar)	P_{CO} (bar)	convn (%)	iso/ n	$k_{n\text{-ald}}$ ($\times 10^3$ mol mol ⁻¹ h ⁻¹)	k_{isoald} ($\times 10^3$ mol mol ⁻¹ h ⁻¹)
66	5	11	11	2.3	2.7	6.3
54–56 ^a	11	11	22	3.3	3.9	12.6
67	17	11	20	4.4	5.5	24.4
68	24	11	21	4.7	8.0	37.8
69	11	5	21	2.0	5.6	11.0
54–56 ^a	11	11	22	3.3	3.9	12.6
70	10	16	23	4.3	3.4	14.8
71	10	21	23	5.0	2.3	11.4
72	10	33	18	4.5	1.3	5.9

^a Average of runs 54, 55, 56 is given, $\sigma(n-1)(\text{TOF}) = 2.00 \times 10^3$.

Figure 4. Dependency of the rate of formation of aldehydes on CO pressure. TOF = turnover frequency, □ = turnover frequency for the branched aldehydes, ▲ = turnover frequency for the normal aldehydes. Conditions: $T = 80$ °C, $P_{\text{H}_2} = 11$ bar, $[\text{Rh}(\text{CO})_2\text{Acac}] = 0.25$ mmol dm⁻³, $[(2\text{-tBu-4-MeC}_6\text{H}_4\text{O})_3\text{P}] = 5$ mmol dm⁻³, $[\text{styrene}] = 0.89$ mol dm⁻³ in 20 mL of toluene.

(Table 9). At temperatures above 80 °C, the observed rate for isoaldehydes remains equal. Remarkably (Table 10), the order in H_2 for the formation of linear aldehydes is lower than 1 and the order in H_2 for the formation of isoaldehydes is larger than 1. This means that the regioselectivity is also dependent on the H_2 pressure; at increasing H_2 pressure the formation of branched aldehyde is more favored. At an increasing CO/H_2 ratio, the hydroformylation reaction is suppressed, the formation of the isoaldehyde being slightly less affected (Table 10). As a result the plot of the rate of formation of branched aldehydes vs CO pressure shows a maximum (Figure 4).

Discussion

Oct-1-ene. The high hydroformylation rates are remarkable. As reported by Jongsma,¹⁵ in competition with CO, only one phosphite coordinates to the Rh center due to its large cone angle (180°, cf. PPh_3 145°).¹⁶ This complex has, similar to the $\text{HRh}(\text{CO})_4$ catalyst, a strong aptitude for CO dissociation compared with the triphenylphosphine-modified catalyst. With only one phosphite bonded to the rhodium, the 16-electron complex easily binds to the olefin, thus initiating a very fast reaction cycle. Due to the large space available in comparison with the $\text{HRh}(\text{CO})_2(\text{PPh}_3)_2$ system, the reaction to the branched aldehyde proceeds with relative ease as well, resulting in a moderate overall linearity.

Another remarkable result is the runaway character of the reaction. This is probably the reason that some other authors^{6,11} postulated that bulky phosphite ligands induce a high isomerization rate and hence are not applicable as modifying ligands in the hydroformylation of terminal alkenes. The hydroformylation reaction proceeds so fast that all CO present in solution is consumed. At very low concentrations of CO, the mass transport is now rate-determining and the system catalyzes isomerization (see also Experimental Section). When all terminal alkenes are converted into aldehydes, the internal alkenes start to participate in the hydroformylation as well. As a result, the high isomerization rates give low n/iso ratios. To circumvent this problem, the reaction rate has to be low or the stirring of the reaction mixture has to be efficient. In our apparatus with magnetic stirring bars, no kinetic measurements could be done at CO pressures below 5 bar and a rhodium concentration above 0.8 mmol dm⁻³, but otherwise stirring was effective.

A first-order dependency in H_2 concentration indicates that the H_2 reaction with the rhodiumacyl intermediate is the rate-determining step. Cavalieri d'Oro and co-workers⁹ found that when propene was hydroformylated with the PPh_3 -modified rhodium carbonyl complex, higher H_2 pressures affect the reaction rate only slightly and the value found for the order in H_2 was between 0.0 and 0.05. Thus, the bulky phosphite system does not resemble the triphenylphosphine-modified catalyst but our reaction appears to fit the kinetics found for the unmodified rhodium carbonyl catalyst by Markó *et al.*³ (eq 1) who used 1-heptene as a substrate and performed the reaction at pressures above 75 bar. We found approximately the same dependency on H_2/CO and Rh, and our initial reaction rate was also independent of the olefin concentration when oct-1-ene was used as a substrate (even at these low concentrations). After 50% conversion or at the corresponding initial oct-1-ene concentrations, the reaction rate becomes dependent on the alkene concentration, but for further considerations we choose to focus on the catalyst behavior at the initial conditions. The only step of the reaction mechanism featuring a reaction with H_2 is the hydrogenolysis of $\text{RC}(\text{O})\text{Rh}(\text{CO})_{4-n}\text{P}_n$ forming the aldehyde and regenerating the starting catalytic active rhodium complex (step 7 in Scheme 2).

The negative order in CO can be due to two steps in the reaction cycle where CO can play an inhibiting role (steps 1 and 6 of Scheme 2). Step 1 can be ruled out

Scheme 2. Proposed Mechanism of the Tris(2-*tert*-butyl-4-methylphenyl) Phosphite Modified Rhodium-Catalyzed Hydroformylation

from any significant importance because the reaction rate is found to be independent of the oct-1-ene concentration (provided that $k_{-1}[\text{CO}] \gg k_2[\text{oct-1-ene}]$).¹⁷ The second step where the presence of a CO molecule can inhibit the reaction is in step 6, after the rhodium acyl complex has been formed. After step 5, two onward reactions are possible. First, reaction with H₂ can take place, which finally results in the starting catalyst complex and product aldehyde. Second, a molecule of CO can occupy the vacant site and a saturated inactive complex is formed, thus inhibiting the completion of the cycle. The order in CO is explained by the equilibrium represented by step 6 in Scheme 2. The resulting negative order in CO suggests that the acyl species rather than the alkyl species is the most abundant species under the reaction conditions; Garland⁶ observed $\text{RC(O)Rh}(\text{CO})_4$ in the system without modifying ligands, and although he used a different substrate, neohexene, he found approximately the same rate equation (zeroth order in substrate concentration). The fact that we found an order in CO that is somewhat larger than -1 (about -0.5 to -1) suggests that certain reaction steps have rates of similar magnitude, which results in a less clear-cut rate equation. It was nearly impossible to derive a useful rate equation comprising all seven steps which can be applied for all substrates,¹⁸ and we are forced to treat the different substrates separately. We start from the experimentally determined concentration dependencies and choose only that part of the scheme that is likely to fit the data (see also cyclohexene discussion).

(17) The *in situ* infrared spectrum during the hydroformylation of oct-1-ene showed a species clearly different from the $\text{HRhP}(\text{CO})_3$ (P = tris(2-*tert*-butyl-4-methylphenyl) phosphite) complex (2093 (w), 2045 (s), and 2016 cm^{-1} (s)), the predominant species expected if the rate-limiting step is the addition of the substrate as indeed occurred when cyclohexene was hydroformylated. The observed carbonyl frequencies during the hydroformylation of oct-1-ene were 1955 (w), 2027 (s), and 2043 (s), and no change occurred when H₂ was replaced by D₂ (conditions: $T = 65^\circ\text{C}$, $P_{\text{H}_2} = 5$ bar, $P_{\text{CO}} = 15$ bar, $[\text{Rh}(\text{CO})_2\text{Acac}] = 3.24 \text{ mmol dm}^{-3}$, $[\text{tris}(2\text{-}i\text{-tert-butyl-4-methylphenyl) phosphite}] = 52.83 \text{ mmol dm}^{-3}$, and $[\text{oct-1-ene}] = 1.04 \text{ mol dm}^{-3}$ in 12 mL of cyclohexane). No acyl CO frequency could be observed probably because (if present) it would absorb in the same region as the aldehyde carbonyl group.

(18) We made an attempt to describe the kinetic behavior with four steps involved. The mechanism was reduced to the following sequence:

With eq a in preequilibrium, employing a steady state approach for $[\text{HRh}(\text{alkene})]$ and $[\text{RhR}]$ and making the assumption that $[\text{Rh}] = [\text{HRh}(\text{CO})] + [\text{HRh}] + [\text{HRh}(\text{alkene})] + [\text{RhR}]$ we obtained the following

For oct-1-ene, the hydrogenolysis is rate-determining (step 7, Scheme 2):

$$r = k_7[\text{RhP}(\text{CO})_2\text{C(O)R}][\text{H}_2] \quad (3)$$

It is assumed that all forward steps are faster and that step 6 is in equilibrium. Furthermore we prefer a preequilibrium treatment rather than a steady state approach since after some time the equilibrium of step 6 will be established. With $[\text{Rh}] \approx [\text{RhP}(\text{CO})_2\text{C(O)R}] + [\text{RhP}(\text{CO})_3\text{C(O)R}]$, the next equation is obtained:

$$r = \frac{k_7[\text{H}_2][\text{Rh}_t]}{K_6[\text{CO}] + 1} \quad (4)$$

When $K_6[\text{CO}] \gg 1$, (4) is reduced to

$$r = \frac{k_7[\text{H}_2][\text{Rh}_t]}{K_6[\text{CO}]} \quad (5)$$

This equation describes the observed first order in H₂ and inverse first order in CO and is indeed similar to that of the unmodified system, eq 1, described by Markó.³

A regularly recurring subject is the selectivity to hydroformylation *vs* isomerization and the normal to branched ratio. The relation between the observed isomerization and the normal to branched ratio has been clearly explained by Lazzaroni.^{19,20} Isomerization is a result of β -hydride elimination of the isoalkyl bonded to the rhodium. The elimination can occur from two different sides of the secondary bonded alkyl forming either 1-alkene or 2-alkene. Because this reaction has a higher free energy of activation than the hydroformylation reaction and because β -hydride elimination requires a vacant site, the proportion of isomerization is expected to increase with higher temperatures and lower pressures. Lazzaroni showed by means of deuterioformylation of hex-1-ene that indeed the degree of isomerization depended on the reaction conditions. No isomerization occurred at low temperatures, and the amount of deuterated rearrangement products was higher for the branched than for the linear metal-alkyl. At a reaction temperature of 100 °C, for linear alkyls, the hydroformylation predominates β -hydride elimination, but for the branched alkyl, elimination predominates hydroformylation. This was also observed for the bulky phosphite system (see Table 2). In the present system the degree of isomerization increases with temperature. Although isomerization of the linear alkyl is not productive, we exclude β -hydride elimination. Otherwise, our kinetic data would be distributed and not give such a clear picture as is shown here; β -hydride elimination of the linear alkyl species would cause a decrease in the overall rate of formation of aldehydes.

equation:

$$r = \frac{K_1 k_2 k_3 k_4 [\text{Rh}_t] [\text{alkene}] [\text{CO}]}{A + B[\text{alkene}] + C[\text{alkene}][\text{CO}] + D[\text{CO}] + E[\text{CO}]^2}$$

with $A = K_1 k_2 k_3$, $B = K_1 k_2 k_3 + K_1 k_2 k_{-3}$, $C = K_1 k_2 k_4$, $D = K_1 k_{-2} k_4 + K_1 k_3 k_4 + k_{-2} k_{-3}$, and $E = k_{-2} k_4 + k_3 k_4$, which reduces under suitable conditions to (a). The total derivation as well as those of the used rate equations are available as supplementary material.

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As only the isoalkylrhodium will form internal alkenes (Scheme 3), the relative amount of branched aldehyde diminishes and the apparent initial normal to branched ratio will be higher, and is indeed the case (see tables). Since 1-alkenes are much more reactive than internal alkenes, significant hydroformylation of the latter will take place only after most of the alk-1-ene has been consumed.

When no β -hydride elimination takes place ($k_3 \gg k_{-3}$), the irreversible step 3 (Scheme 2) determines the regioselectivity and yet the hydrogenolysis step 7 (Scheme 2) is rate-determining. When the substrate conversion is high and the conditions are chosen such that step 3 (Scheme 2) is only reversible for 2-alkyl intermediates, the isomerization products are hydroformylated and the regioselectivity depends on the degree of conversion. The kinetics of the internal alkenes are different, as now coordination of alkene to rhodium (step 2) is rate-determining.

Cyclohexene. A first-order dependency in cyclohexene concentration, a negative order in CO, and a very slightly positive order in H_2 leads to the conclusion that the rate-determining step is no longer the hydrogenolysis reaction (Scheme 2, step 7) as was found for oct-1-ene. The data clearly indicate that one of the steps preceding step 7 is now rate-determining. Most likely, the exchange of one CO ligand for cyclohexene (Scheme 2, step 2) is the slowest step. Due to its internal double bond cyclohexene approaches the rhodium center less easily, *i.e.*

$$r = k_2[\text{RhH}][\text{cyclohexene}] \quad (6)$$

From the assumption that $\text{RhP}(\text{CO})_3\text{H}$ and $\text{RhP}(\text{CO})_2\text{H} + \text{CO}$ occur in preequilibrium and $[\text{Rh}_t] = [\text{RhP}(\text{CO})_2\text{H}] + [\text{RhP}(\text{CO})_3\text{H}]$, it follows that

$$r = \frac{K_1 k_2 [\text{Rh}_t][\text{cyclohexene}]}{K_1 + [\text{CO}]} \quad (7)$$

This relation describes both the observed orders in the rhodium precursor and cyclohexene and the negative order in CO. The kinetic expression would also be in accordance with step 3 being the rate-determining step following a fast preequilibrium of steps 1 and 2. However, this seems unlikely since upon migration (Scheme 2, step 3) the steric repulsion is released.

Our results are not completely in agreement with the kinetic results that Markó obtained with the rhodium carbonyl system. He observed an equal dependence in the cyclohexene concentration but he did not notice any influence of the CO partial pressure, for which we found an order between -0.6 and -0.7 . This can be due to the different nature of the active complexes $\text{HRh}(\text{CO})_4$ and $\text{HRhP}(\text{CO})_3$ ($P = \text{tris}(2\text{-tert-butyl-4-methylphenyl})\text{phosphite}$). Furthermore, $\text{HRh}(\text{CO})_4$ is in equilibrium with a tetrameric rhodium cluster. The complexes may have a different aptitude for CO dissociation resulting in a different overall kinetic equation. Little mechanistic research has been done on the triphenylphosphine-modified rhodium-catalyzed hydroformylation of cyclic alkenes because of their poor reactivity,²¹ but it

would seem that also for these catalysts the association of metal and alkene is rate-determining.

Styrene. The hydroformylation of styrene with the bulky phosphite modified catalyst is somewhat slower than that of oct-1-ene. This is in contrast with results obtained with $\text{Rh}_4(\text{CO})_{12}$ and $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ as catalyst. With $\text{Rh}_4(\text{CO})_{12}$ as the catalyst, styrene reacted more than twice as fast ($124 \times 10^3 [\text{mol}] [\text{min}]^{-1}$ for styrene *vs* $50.1 \times 10^{-3} [\text{mol}] [\text{min}]^{-1}$ for oct-1-ene, $5.3 \times 10^{-2} \text{ mM } \text{Rh}_4(\text{CO})_{12}$, 75°C , $P = 130 \text{ bar}$).²² With the triphenylphosphine-modified catalyst, styrene reacted somewhat faster than the unsubstituted 1-alkenes as hex-1-ene, hept-1-ene, and dodec-1-ene²³ (styrene: 2.8 cycles/h *vs* hex-1-ene and hept-1-ene 2.3 and dodec-1-ene 2.0 cycles/h, 2.5 mM catalyst concentration, 1.0 M substrate in benzene, 25°C , 0.7 bar, $\text{CO}/\text{H}_2 = 1$) although comparison were is difficult because of the different kinetic expression found for this catalyst system. The lower rate of the bulky phosphite catalyst for styrene *vs* 1-octene cannot be assigned to the larger phenyl substituent at the alkene, since the addition of alkene to rhodium does not show up in the rate equation; also in the report of Lazzaroni²³ the rate of styrene conversion is independent of the styrene concentration in the range of 0.4 to 2.4 mol dm^{-3} (180 bar, 90°C , $\text{Rh}_4(\text{CO})_{12}$ catalyst). It is also unlikely that the hydrogenolysis reaction would strongly depend on the nature of the organic fragment of the rhodium acyl group (respectively 1-nonanoyl, 2-methyloctanoyl, 2-phenylpropanoyl, 3-phenylpropanoyl), although a slightly different rate (k_7 and K_6) for the 2-phenylpropanoyl might be expected. In the extreme situation, with reaction 7 (Scheme 2) being rate-determining, the iso/normal product distribution reflects the concentrations of the iso and normal acyl species, which on their turn are determined by the rates of the insertion reactions (step 3, Scheme 2) leading to the iso and normal alkyl species, provided that these reactions are irreversible. Since the overall reaction rate is independent of styrene concentration but lower than that of oct-1-ene, and since the hydrogenolysis rate and K_6 are expected to be of similar magnitude, we conclude that the concentrations of the acylrhodium species with styrene are lower than those with oct-1-ene in the concentration regime studied here. In other words, rhodium does not reside completely in the acyl stage (as it does with oct-1-ene), but it does not reside in the hydride stage either (as it does with cyclohexene or cyclooctene).¹⁵ The product distribution and its dependency on the CO pressure hint as to the explanation of these phenomena.

Deuterioformylation of styrene at 60°C ²⁴ has been shown to involve an irreversible alkene insertion step. The iso to normal ratio reported was 15 (180 bar). At higher temperatures the iso/*n* ratio decreases (*i/n* = 5 at 90°C , total pressure = 180 bar). The present rhodium catalyst modified with a bulky phosphite gives a lower iso/*n* ratio (10.6 at 51°C , 2.1 at 90°C , total pressure = 22 bar). We presume that also in this instance the styrene insertion is irreversible. The isomer ratio reflects the preference of the styrene insertion reaction, modified by small differences in the

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Scheme 3. Possible Reactions for the Styrene-Coordinated Rhodium Complex

rate constants that may follow this step. For oct-1-ene the ratio iso/*n* is 0.7, *i.e.* considerably lower than for styrene. The strong preference of styrene to form the branched alkyl species (1-phenylethyl, Scheme 3, 4) must be related to the resonance-stabilized species (Scheme 3, 5) suggested before in 1974 by Tanaka *et al.*²⁵ and in 1983 by Tolman and Faller.²⁶ These kinds of benzyl complexes are known for rhodium²⁷ and platinum.²⁸ After the migratory insertion, a coordinatively and electronically unsaturated metal complex is formed. For 1-phenylethyl, however, this unsaturation is released by coordination in an η^3 -fashion (5). The relative stability of this species is crucial in styrene carbonylation and hydroformylation, *e.g.* insertion of styrene into a palladium acetyl bond gives an η^3 -bonded 1-phenylethyl group.²⁹ Depending upon the conditions of the rhodium-catalyzed hydroformylation of styrene, a substantial amount of the rhodium complex may reside in this η^3 -1-phenylethyl state. When migratory insertion of an alkene into rhodium hydride leads to an η^2 -alkylrhodium species (1-octyl, 2-methylheptyl, 2-phenylethyl, Scheme 3, 2), the vacant site will be occupied by carbon monoxide or phosphine ligand with a high rate; under these reaction conditions the insertion is now irreversible and the regioselectivity of the reaction has been determined. The η^3 -1-phenylethyl species (Scheme 3, 5) remains in a state that may easily undergo deinsertion.

Ojima³⁰ presented a different explanation for the higher selectivity toward the branched aldehyde. When electron-withdrawing substituents are involved, the C_α -metal bond of a π -olefin complex should be stronger than

the C_β -metal bond, resulting in a preferred migration of the hydride to the C_β forming an isoalkyl metal species. According to the author, the normal to branched aldehyde ratio reflects the ratio of the isoacyl and *n*-acyl metal species provided that the hydrogenolysis is not rate-determining. If hydrogenolysis is the rate-determining step, isomerization of the acyl metal complexes can occur, giving rise to an increased iso/*n* aldehyde ratio.³⁰ Although an (η^3 -1-phenylethyl)rhodium species was never observed during a catalytic reaction, the recent results of Lazzaroni about the extreme susceptibility of the 1-phenylethyl intermediate toward β -hydride elimination support the occurrence of the η^3 -1-phenylethyl compound.

From the reaction data it becomes immediately clear that more so than for oct-1-ene, the β -hydride elimination is a crucial step in determining the product distribution. For styrene, however, the progress of this reaction cannot be established by the presence of isomerization products. As for oct-1-ene, β -hydride elimination has a higher free energy of activation than the hydrogenolysis reaction at the end of the hydroformylation cycle. As a result, the proportion of β -hydride elimination increases with temperature. The branched alkyl species, in this instance 1-phenylethyl, is more sensitive to elimination than the linear alkyl species and hence the observed linearity of the product increases, as was clearly pointed out by Lazzaroni.^{19,20} The results with bulky phosphite rhodium catalysts fit perfectly well with those obtained with rhodium carbonyl catalysts, although the latter are slower.

the importance of intermediate 5 is also expressed in the ratio of the formation of branched and linear products as a function of H_2 and CO pressures (Figure 4, Table 10). The first-order dependency of the rate of formation of linear aldehyde (3-phenylpropanal) on H_2 pressure indicates that the hydrogenolysis of the acyl complex (Scheme 2, step 7) is rate-determining. The turnover frequency (TOF) to the branched aldehyde (2-phenylpropanal) shows an observed reaction order in H_2 slightly higher than 1. The reaction rates do not exceed those of oct-1-ene. We explain this as follows. The rate-determining step is again the hydrogenolysis reaction (Scheme 2, step 7) but upon depletion of the acyl species the branched one can be replenished at a higher rate because of the reservoir of 5 and the fast reaction 3 (Scheme 2) leading to 5. In other words the ratio of the concentrations of the rhodium acyl and η^3 -1-phenylethyl species changes with the syngas pressure, and a rigid treatment with reaction 7 (Scheme 2) as being rate-determining is no longer valid. The dependency on CO pressure is more instructive. The rate of formation of 3-phenylpropanal decreases proportionally with the inverse of the CO pressure. Again this is the same as found for the kinetics of the reaction of oct-1-ene to nonanal. Interestingly, the rate of formation of 2-phenylpropanal increases when the CO pressure is raised from 5 to 16 bar ($pH_2 = 11$ bar, 80 °C) and decreases again when the pressure is raised from 16 to 33 bar (Figure 4). The initial increase is caused by the conversion of 5 to the corresponding acyl species; a higher concentration of the acyl species gives a higher overall rate of reaction. When most of the rhodium rests in the acyl state, a further increase of the CO pressure

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cannot lead to further acceleration, instead the "normal" inhibition via equilibrium 6 becomes dominating.

The influence of the CO pressure on the rate of the formation of the branched product clearly explains why the product ratios in literature data of styrene hydroformylation depend so strongly on the pressure. If both modes of styrene insertion are irreversible (low temperature, high CO pressure, high ligand concentration), the iso/*n* ratio is very high (10–25) (case 1). Conditions can be set such that only the formation of the linear (2-phenylethyl)rhodium complex is irreversible. Now, kinetically, a highly linear product can be produced (case 2). A third possibility arises when all reactions 1–6 are reversible and yet reaction 7 (Scheme 2) is rate-determination. In this instance (case 3) the normal to branched ratio is determined by the ratio of the concentrations of the equilibrated acyl species.

Looking at these mechanistic considerations, it is clear that neither the kinetic expression for oct-1-ene nor the expression for cyclohexene is suitable for the styrene substrate. An analytic expression taking into account all reactions describing these features would be rather complicated.¹⁸

Conclusions

In general, the tris(2-*tert*-butyl-4-methylphenyl) phosphite modified rhodium hydroformylation catalyst is an excellent catalyst, particularly for unsubstituted alk-1-enes, yielding high rates under mild conditions.

The catalyst system exhibits simple kinetics for oct-1-ene and cyclohexene while those for styrene are more complicated. The kinetics of oct-1-ene and cyclohexene resemble those of the $\text{Rh}_4(\text{CO})_{12}$ system as studied by Markó and are clearly different from the triphenylphosphine-modified rhodium catalyst. The kinetics of oct-1-ene are reduced to a simple equation by virtue of the relative inertness of the isomerization product. Reaction 3 of Scheme 2 is irreversible under the conditions studied, while reaction 7 is rate-determining. As a result the regioselectivity is determined in step 3, and beyond this step no normal to iso equilibration takes place.

For cyclohexene, the rate-limiting step lies at the beginning of the cycle; the initial reaction of the alkene with the rhodium hydride species is the slowest step.

For styrene, in contrast to oct-1-ene, β -hydride elimination has an important influence on the regioselectivity; the selectivity for the branched product increases at lower temperatures and higher pressures.

Experimental Section

General Information. All preparations were carried out under an atmosphere of nitrogen or argon by using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone prior to use. Oct-1-ene was distilled from sodium; cyclohexene and styrene were percolated over neutral alumina. $\text{Rh}(\text{CO})_2\text{Acac}$ was purchased from Johnson Matthey and trimethyl phosphite from Aldrich and both were used as received. Gas-liquid chromatography analyses were done using a DB 5 column and a Carlo Erba GC 6000Vega series 2 chromatograph. NMR measurements were performed on a Bruker AC 100 or AMX 300 spectrometer. Chemical shifts are given in ppm using TMS or H_3PO_4 as standard.

Hydroformylation studies were performed in a stainless steel autoclave (181 mL) containing a glass beaker. The

Figure 5. Dependency of the turnover frequency (TOF) isomerization and regioselectivity on the stirring rate. ♦ = $\text{TOF}/(1000 \text{ mol } [\text{mol Rh}]^{-1} \text{ h}^{-1})$, × = % isomerization products, □ = *n*/*i* ratio. Conditions: $T = 80^\circ\text{C}$, $P_{\text{H}_2} = P_{\text{CO}} = 10 \text{ bar}$, $[\text{Rh}(\text{CO})_2\text{Acac}] = 0.1 \text{ mmol dm}^{-3}$, $[(2\text{-tBu-4-MeC}_6\text{H}_4\text{O})_3\text{P}] = 5 \text{ mmol dm}^{-3}$, $\text{P/Rh} = 50$, $[\text{oct-1-ene}] = 0.86 \text{ mol dm}^{-3}$ in 20 mL of toluene.

autoclave is magnetically stirred and equipped with a reservoir, a pressure transducer, a thermocouple, and a sampling device. The beaker was charged with the rhodium precursor ($\text{Rh}(\text{CO})_2\text{Acac}$), the tris(2-*tert*-butyl-4-methylphenyl) phosphite, and an internal standard (decane) and filled with toluene up to 20 mL. The autoclave with the beaker was closed and flushed several times with CO/H_2 and was brought under pressure. After the catalyst solution was heated, the substrate was charged to the reservoir and added to the reaction mixture by overpressure. Upon this addition, the reaction started immediately as was evidenced by a pressure drop and an increase of the temperature. Attention was paid to the gas consumption at 30% conversion; at the given alkene concentration and gas volume, less than 10% of the gases was consumed. During the reaction, a number of samples were taken and immediately quenched (by $\text{P}(\text{OMe})_3$) so that a catalytically inactive rhodium complex was formed. These samples were analyzed by GC. The reaction rates for oct-1-ene and styrene are represented by the turnover frequencies (TOF), i.e. the total amount of formed aldehydes recalculated to moles of aldehydes per mole of rhodium per hour. The zeroth-order dependence of the reaction rate of the substrate concentration allowed us to average the TOFs over the reaction time. The tables were composed using samples with similar conversions. For cyclohexene, a different order in the substrate concentration was observed and the k_0 of the reaction could be determined. During the reaction, several averaged turnover frequencies were calculated from the observed decrease in CO/H_2 pressure. These data were used to obtain a plot of the $\ln(\text{TOF})$ vs reaction time. Extrapolation of the calculated line produced the k_0 of the reaction.

To exclude a diffusion-limited reaction, we carried out experiments in which we varied the stirring velocity. Figure 5 shows that at very low stirring speeds or with no stirring at all, the reaction is diffusion-limited and at increasing velocity the reaction rate eventually remains constant. Up to 100 rpm, the turnover frequency deviates during the reaction, so average values are presented here. Furthermore at low stirring rates the isomerization rate is somewhat higher; at 100 rpm 10.8% isomerized oct-1-ene is formed and from 900 rpm the amount of isomerized oct-1-ene stays around 2%. Consequently the percentage of linear aldehydes is somewhat lower at high stirring rates (a very slight change was obtained; the *n*/*i* decreased from 2.10 to 1.91). We worked at a stirring rate of 1100 rpm, situated in the adequate region. At the extremely low rhodium concentrations applied and our standard reaction conditions it is not likely that the reaction rate is limited by

mass transfer. As we work with 2 μ mol of rhodium precursor, the overall gas consumption will be low in spite of the high TOF's.

Preparation of Tris(2-*tert*-butyl-4-methylphenyl) Phosphite. PCl_3 (10.1 g, 73.3 mmol) was added dropwise under stirring at 70 °C to 48.15 g (293.1 mmol) of 2-*tert*-butyl-4-methylphenol in 30 mL of toluene. When all PCl_3 was added, the mixture was heated slowly (in 30 min) to 150 °C and stirred at this temperature for 3 h. Meanwhile, the formed HCl was removed several times by evacuating the mixture. After being cooled to 70 °C, the mixture was again evacuated for 15 min. The product was precipitated by addition of 100 mL of $\text{CH}_3\text{-}$

CN. The precipitate was filtered off and washed with 100 mL of CH_3CN . The product was purified by recrystallization from toluene/ CH_3CN . Yield: 23.26 g (61%) of white crystals. ^{31}P NMR (CDCl_3): δ 131 ppm. ^1H NMR (CDCl_3): δ 1.4 ppm (s, 9H, tBu), 2.3 (s, 3H, Me), 7.1. (m, 3 H, aromatic). Mp: 111 °C.

Supplementary Material Available: Total derivation of equations in ref 18 and the rate equations used (4 pages). Ordering information is given on any current masthead page.

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