Diphosphine–Rhodium Complex-Catalyzed Hydroformylation of α,β-Unsaturated Esters

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The product distribution in the hydroformylation of α,β-unsaturated esters (ethyl acrylate, methyl methacrylate, methyl crotonate, and methyl tiglate) catalyzed by $Rh_2Cl_2(CO)_4$ was studied at 150 °C under 100 atm of synthesis gas ($CO/H_2=1/1$) in the absence or presence of various additional phosphorus ligands. In order to attain a high selectivity of α-formylation (>80%), the addition of shorter methylene-chained diphosphines ($R_2P(CH_2)_nPR_2$, R=phenyl or cyclohexyl, $n=2$—4) to the reaction system was essential, while the use of $Rh_2Cl_2(CO)_4$ alone or in combination with triphenylphosphine or a longer diphosphine, $Ph_2P(CH_2)_5PPh_2$, resulted in a very low α-selectivity. The effects of the reaction variables on the product distribution were also examined for acrylate and methacrylate using $Ph_2P(CH_2)_4PPh_2$ and $Ph_2P(CH_2)_2PPh_2$, respectively, as additional ligands.

Among many types of polar olefins, α,β-unsaturated esters have received much attention as substrates for hydroformylation. The selective β-formylation of the ethylenic linkage of acrylates, followed by cyclization to afford γ-butyrolactone, has been accomplished by the use of a cobalt carbonyl catalyst.[1] On the other hand, it has been noted in a patent claim that a rhodium catalyst favors α-formylation, though the selectivity attained is not very high.[2] The composition of the products from ethyl acrylate under a wide range of the reaction conditions has also been examined in detail by the use of cobalt[3] as well as rhodium catalyst.[4] In the hydroformylation of methyl methacrylate by a rhodium catalyst, the addition of a large amount of a phosphorus ligand to the reaction system or a much elevated pressure of synthesis gas as high as 1000 atm is required for selective α-formylation.[5,6] Methyl crotonate undergoes formylation mainly on the β-carbon, and a relatively large amount of the hydrogenation by-product is also formed.[5]

In this report, the authors will describe the hydroformylation of various α,β-unsaturated esters by the use of the diphosphine–rhodium catalyst system, and it will be shown that this catalyst system is extremely efficient for selective α-formylation.

Experimental

Materials. Benzene and ethylbenzene were distilled under nitrogen. All of the substrates were commercial products, and were freshly distilled under nitrogen of a reduced pressure before use. Triphenylphosphine and 1,2-bis(diphenylphosphino)ethane were used as purchased. Tetracarbonyldi-μ-chlorodirhodium,[7] 1,3-bis(diphenylphosphino)propane,[8] 1,4-bis(diphenylphosphino)butane,[9] 1,5-bis(diphenylphosphino)pentane,[9] 1,2-bis(dicyclohexylphosphino)ethane,[10] 1,4-bis(dicyclohexylphosphino)butane,[11] and 1,2-bis(5*H*-dibenzophospholyl)ethane[12] were prepared by the previously reported methods.

Reaction Procedure. A 37-ml Schlenk-tube-type high-pressure reaction vessel, made of stainless steel (SUS 316), was charged under a nitrogen atmosphere with 3 ml of a solvent (ethylbenzene for ethyl acrylate and benzene for the other substrates), 1.3 mg of tetracarbonyldi-μ-chlorodirhodium (6.7×10^{-6} mol with respect to the rhodium atom), a desired amount of a phosphine, and 1.5 ml of a substrate. The reaction vessel was then sealed and flushed with carbon monoxide. Then, carbon monoxide and hydrogen were introduced up to their given partial pressures. The temperature was elevated in an oil bath. The reaction solution was then agitated magnetically.

Analysis of the Products. An aliquot of the reaction mixture was analyzed by gas chromatography. A Shimadzu model GC-3B gas chromatograph, equipped with a stainless steel column packed with diethylene glycol succinate polyester on Neopak AS (3 mm i.d.×2.5 m) was used at an oven temperature of 120 °C for most cases. The remainder of the reaction mixture was submitted to distillation, and the products were identified spectroscopically. The IR and NMR spectra were recorded on a Shimadzu IR 27G apparatus, and a JEOL C-60HL apparatus, respectively.

Results

The reaction was carried out at 150 °C under 100 atm of synthesis gas ($CO/H_2=1/1$), with $Rh_2Cl_2(CO)_4$ as a catalyst precursor, in the absence or presence of a variety of phosphines. The phosphorus-to-rhodium ratio of 4 : 1 was used in every case. The boiling points and spectral data of the products are summarized in Table 1. The NMR spectra of some α-formylated isomers show that these isomers are present in equilibrium with the corresponding enol forms. The approximate ratio of enol to aldehyde under the conditions of the NMR measurement (carbon tetrachloride solution, 31.5 °C) is also shown in the table.

Hydroformylation of Ethyl Acrylate. The results are summarized in Table 2. The catalytic activity of the rhodium complex was, in the absence of a phosphine, very low, and ethyl β-formylpropionate was mainly formed. The addition of triphenylphosphine to the reaction system much improved the α-selectivity, though the reaction was still sluggish. In contrast, when carried out in the presence of α,ω-bis(diphenylphosphino)-alkanes, $Ph_2P(CH_2)_nPPh_2$ ($n=2$—4), the reaction proceeded extremely fast, and the α-carbon was formylated almost exclusively. It was also found that the extent of the competitive hydrogenation was enhanced by the use of these diphosphines. As the carbon chain between the two phosphorus atoms of the diphosphine got longer from C_2 to C_4, the amount of the hydrogenation by-product much decreased and the α-selectivity became slightly higher. However, when the still longer diphosphine, $Ph_2P(CH_2)_5PPh_2$, was used, a very low α-selectivity was caused, and the competitive hydrogenation intensively occurred again. In addition, a much

TABLE 1. BOILING POINTS AND SPECTRAL DATA OF THE REACTION PRODUCTS

Structure	Bp (°C/Torr)	IR[a] (cm^{-1})	^{1}H-NMR[b] (τ ppm)	Enol / Aldehyde
$CH_3CHCOOCH_2CH_3$ (CHO)			0.36 (1H, d, J=1.4 Hz, CHO), 5.83 (2H, q, CH_2), 6.72 (1H, dq, CH), 8.75 (3H, d, J=7.2 Hz, CH_3CH), 8.75 (3H, t, J=6.9 Hz, CH_3CH_2)	
CH_3-C(=CH-OH)-$COOCH_2CH_3$	47.0—49.5/10	2730 ($\nu_{C(=O)H}$), 1745, 1720, 1668 (ν_{CO}), 1616 ($\nu_{C=C}$)	−1.21 (1H, d, OH), 3.09 (1H, d, J=12.6 Hz, CH), 5.81 (2H, q, CH_2), 8.35 (3H, s, CH_3C=), 8.73 (3H, t, J=6.7 Hz, CH_2CH_3) 0.35 (1H, s, CHO), 5.87 (2H, q, CH_2CH_3)	1.7/1.0
$OHC-CH_2CH_2COOCH_2CH_3$	56.5—57.3/3	2820, 2715 ($\nu_{C(=O)H}$), 1730 (ν_{CO})	7.15—7.55 (4H, m, $2CH_2$), 8.75 (3H, t, J=7.0 Hz, CH_3)	
$(CH_3)_2CCOOCH_3$ (CHO)	41.0—42.5/12	2820, 2710 ($\nu_{C(=O)H}$), 1730 (ν_{CO})	0.48 (1H, s, CHO), 6.28 (3H, s, OCH_3), 8.71 (6H, s, $2CH_3$)	
$OHC-CH_2CHCOOCH_3$ (CH_3)	49.0—49.3/3	2825, 2720 ($\nu_{C(=O)H}$), 1730 (ν_{CO})	0.36 (1H, s, CHO), 6.38 (3H, s, OCH_3), 7.0—7.6 (3H, m, $CHCH_2$), 8.82 (3H, d, J=7.0 Hz, $CHCH_3$)	
$CH_3CH_2CHCOOCH_3$ (CHO)			0.36 (1H, d, J=2.1 Hz, CHO), 6.25 (3H, s, OCH_3), 6.83 (1H, dt, CH), 8.10 (2H, m, CH_2), 9.06 (3H, t, J=7.5 Hz, CH_3CH_2)	1/1
CH_3CH_2-C(=CH-OH)-$COOCH_3$	43.0—46.0/10	2710 ($\nu_{C(=O)H}$), 1730, 1666 (ν_{CO}), 1605 ($\nu_{C=C}$)	−1.22 (1H, d, OH), 3.01 (1H, d, J=12.5 Hz, CH), 6.22 (3H, s, OCH_3), 8.04 (2H, q, CH_2CH_3), 9.00 (3H, t, J=7.5 Hz, CH_3CH_2)	
$CH_3CHCH_2COOCH_3$ (CHO)	49.0—51.0/3	2800, 2700 ($\nu_{C(=O)H}$), 1730 (ν_{CO})	0.41 (1H, s, CHO), 6.35 (3H, s, OCH_3), 8.1—8.8 (3H, m, $CHCH_2$), 8.85 (3H, d, J=7.4 Hz, CH_3CH)	
$OHC-(CH_2)_3COOCH_3$	—	2810, 2700 ($\nu_{C(=O)H}$), 1730 (ν_{CO})	0.35 (1H, t, J=1.5 Hz, CHO), 6.38 (3H, s, OCH_3), 7.3—8.3 (6H, m, $3CH_2$)	
$CH_3CH_2C(CH_3)(CHO)COOCH_3$	33.0—36.0/3	2815, 2715 ($\nu_{C(=O)H}$), 1720 (ν_{CO})	0.42 (1H, s, CHO), 6.31 (3H, s, OCH_3), 8.19 (2H, m, CH_2), 8.77 (3H, s, CCH_3), 9.14 (3H, t, J=7.5 Hz, CH_3CH_2)	

a) Neat. b) In a carbon tetrachloride solution (10—20% solution); internal standard: TMS.

TABLE 2. HYDROFORMYLATION OF ETHYL ACRYLATE[a]

Phosphine	Reaction time (min)	Conversion (%)	Product distribution (%)[b]			α-Selectivity (%)[c]
			α	β	Dihydro	
—	36	6	28.6	66.7	4.8	22.9
PPh_3	180	27	71.5	27.0	1.5	72.5
$Ph_2P(CH_2)_2PPh_2$	42	100	64.2	2.6	32.0	96.1
$Ph_2P(CH_2)_3PPh_2$	22	≈100	72.3	2.9	24.8	96.1
$Ph_2P(CH_2)_4PPh_2$	5	≈100	85.4	2.3	12.3	97.4
$Ph_2P(CH_2)_5PPh_2$	550	≈100	49.9	17.0	33.1	74.6
$Cy_2P(CH_2)_2PCy_2$	7	100	79.9	3.8	16.3	95.5
$Cy_2P(CH_2)_4PCy_2$	12	≈100	67.2	1.1	31.7	98.4
DBP-$(CH_2)_2$-DBP[d]	76	100	32.1	17.3	50.5	65.0

a) Reaction conditions: 150 °C, 100 atm (CO/H_2=1/1), phosphorus/rhodium=4/1. b) α, β and dihydro stand for ethyl α-formylpropionate, ethyl β-formylpropionate, and ethyl propionate, respectively. c) α-Selectivity denotes $100\times\alpha/(\alpha+\beta)$. d) DBP stands for the 5*H*-dibenzophospholyl group.

longer reaction time was required for complete conversion in the case of this diphosphine.

The electronic effects on the product distribution were examined by the use of dicyclohexylphosphino analogues of 1,2-bis(diphenylphosphino)ethane and 1,4-bis(diphenylphosphino)butane. These effects are apparently not separable from steric effects, and no clear trends in either the reaction rate or the extent of the competitive hydrogenation could be found. The α-selectivity remained practically unchanged upon the exchange of the phenyl groups for the cyclohexyl ones.

The effect of the structure of the diphosphine was further studied using 1,2-bis(5H-dibenzophospholyl)-ethane, some rhodium complexes of which efficiently catalyzed the hydroformylation of olefinic hydrocarbons.[13] However, for ethyl acrylate, this diphosphine was much inferior in its catalytic activity as well as in its α-selectivity to 1,2-bis(diphenylphosphino)ethane.

Hydroformylation of Methyl Methacrylate. The results of the hydroformylation of methyl methacrylate are collected in Table 3. Unlike ethyl acrylate, methyl methacrylate was rapidly hydroformylated in the absence of phosphines. The β-isomer was mainly formed, accompanied by a considerable amount of the hydrogenation by-product. The addition of tertiary phosphines to the reaction system much retarded the reaction and increased the content of the α-isomer. In addition, it suppressed the competitive hydrogenation except the reaction with 1,3-bis(diphenylphosphino)-propane. The highest α-selectivity accomplished by the use of 1,2-bis(diphenylphosphino)ethane, 81.4%, was lower than that observed in the reaction of ethyl acrylate, probably because of the steric hindrance of the α-methyl substituent. 1,2-Bis(dicyclohexylphosphino)ethane and 1,4-bis(dicyclohexylphosphino)butane, which caused high α-selectivities similar to the diphenylphosphino counterpart in the reaction of ethyl acrylate, gave inferior results for methyl methacrylate. Probably, this is also attributable to the steric hindrance due to the presence of the α-methyl substituent on the double bond as well as to the large ligand cone angle[14] of the bis(dicyclohexylphosphino)alkanes.

Hydroformylation of Methyl Crotonate. The results are shown in Table 4. In comparison with the reactions of ethyl acrylate and methyl methacrylate, the hydroformylation of methyl crotonate gave very diverse results for the product distribution depending on the nature of the added ligands. Competitive hydrogenation was often the main reaction. Nevertheless, some of the diphosphines, such as $Ph_2P(CH_2)_{2(or\ 4)}PPh_2$ and $Cy_2P(CH_2)_2PCy_2$, showed high α-selectivities, suppressing the formation of the β- and γ-isomers which were the main products when the reaction was carried out either in the absence of any additional ligands or in the presence of triphenylphosphine.

Hydroformylation of Methyl Tiglate. The results

Table 3. Hydroformylation of methyl methacrylate[a]

Phosphine	Reaction time (min)	Conversion (%)	Product distribution (%)[b]			α-Selectivity (%)[c]
			α	β	Dihydro	
—	16	100	7.2	73.4	19.6	8.7
PPh_3	200	100	38.5	56.1	5.4	40.8
$Ph_2P(CH_2)_2PPh_2$	105	100	79.5	17.6	2.9	81.8
$Ph_2P(CH_2)_3PPh_2$	250	51	45.9	17.5	36.6	72.4
$Ph_2P(CH_2)_4PPh_2$	360	92	75.5	19.2	5.3	79.8
$Ph_2P(CH_2)_5PPh_2$	420	98	14.7	74.3	11.0	16.5
$Cy_2P(CH_2)_2PCy_2$	450	98	50.2	44.7	5.1	52.9
$Cy_2P(CH_2)_4PCy_2$	280	98	54.9	40.5	4.7	57.6

a) Reaction conditions: 150 °C, 100 atm ($CO/H_2=1/1$), phosphorus/rhodium=4/1. b) α, β and dihydro stand for methyl α-formylisobutyrate, methyl β-formylisobutyrate, and methyl isobutyrate, respectively. c) α-Selectivity denotes $100\times\alpha/(\alpha+\beta)$.

Table 4. Hydroformylation of methyl crotonate[a]

Phosphine	Reaction time (min)	Conversion (%)	Product distribution (%)[b]				α-Selectivity (%)
			α	β	γ	Dihydro	
—	160	100	0.0	51.7	30.0	18.0	0.0
PPh_3	210	100	17.2	52.6	12.6	17.6	20.9
$Ph_2P(CH_2)_2PPh_2$	150	100	22.9	2.0	0.0	75.1	91.8
$Ph_2P(CH_2)_3PPh_2$	210	93	8.8	4.6	0.0	86.6	65.5
$Ph_2P(CH_2)_4PPh_2$	240	92	80.1	5.2	0.0	14.7	93.9
$Ph_2P(CH_2)_5PPh_2$	360	94	3.6	40.6	27.9	28.0	5.0
$Cy_2P(CH_2)_2PCy_2$	360	71	43.5	2.6	0.1	53.8	94.2
$Cy_2P(CH_2)_4PCy_2$	210	40	41.4	28.2	4.7	25.7	55.7

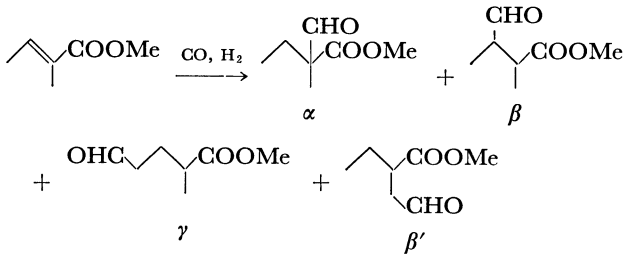
a) Reaction conditions: 150 °C, 100 atom ($CO/H_2=1/1$), phosphorus/rhodium=4/1. b) α, β, γ, and dihydro stand for methyl α-formylbutyrate, methyl β-formylbutyrate, methyl γ-formylbutyrate, and methyl butyrate, respectively. c) α-Selectivity denotes $100\times\alpha/(\alpha+\beta+\gamma)$.

TABLE 5. HYDROFORMYLATION OF METHYL TIGLATE[a)]

Phosphine	Reaction time (h)	Conversion (%)	Yield[b)] (%)	α-Selectivity (%)[c)]
—	5	≈100	44	1.8
$Ph_2P(CH_2)_2PPh_2$	24	24	19	74.9
$Ph_2P(CH_2)_4PPh_2$	24	16	12	73.4

a) Reaction conditions: 150 °C, 100 atm ($CO/H_2=1/1$), phosphorus/rhodium=4/1. b) Total yield of the four aldehydes based on the amount of methyl tiglate charged (see the text). c) α-Selectivity denotes the percentage of methyl α-formyl-α-methylbutyrate in the total amount of the four aldehydes formed.

are shown in Table 5. Unlike the other substrates examined, a significant amount of unidentified high boiling by-product(s) was formed, especially in the absence of phosphine. As concerns the aldehyde formation, after comparing the gas chromatogram of the reaction mixture with that of methyl crotonate, the authors presume that all of the possible four isomeric aldehydes were produced. However, only the α-isomer could be isolated and identified. The other isomers could not be separated in a pure state because of the similarity of their boiling points. The α-selectivity, which was very low without added phosphines, was markedly enhanced by the use of the diphosphines.



Effects of the Reaction Variables. Tables 2 and 3 show that 1,4-bis(diphenylphosphino)butane and 1,2-bis(diphenylphosphino)ethane are the most beneficial α-formylating ligands for ethyl acrylate and methyl methacrylate respectively. Therefore, using those most beneficial combinations of the ligand and the substrate, the effects of the reaction variables, such as the phosphorus-to-rhodium ratio, the reaction temperature, and the partial pressures of carbon monoxide and hydrogen, on the product distribution were briefly examined in order to search for the optimum conditions for selective α-formylation and to shed more light on the role of the diphosphines during the course of the reaction. The results are illustrated in Figs. 1—5.

Figure 1 shows that, in the reaction of ethyl acrylate, the decrease in the amount of the diphosphine slightly lowered the α-selectivity. Competitive hydrogenation was almost completely inhibited at phosphorus-to-rhodium ratios smaller than 2. A similar but more profound influence on the α-selectivity was also observed for methyl methacrylate (Fig. 2), while the effect on the hydrogenation by-product formation was just the reverse of that with ethyl acrylate, and, at the ratio of 2, the extent of hydrogenation was markedly intensive.

Lowering the reaction temperature increased the α-

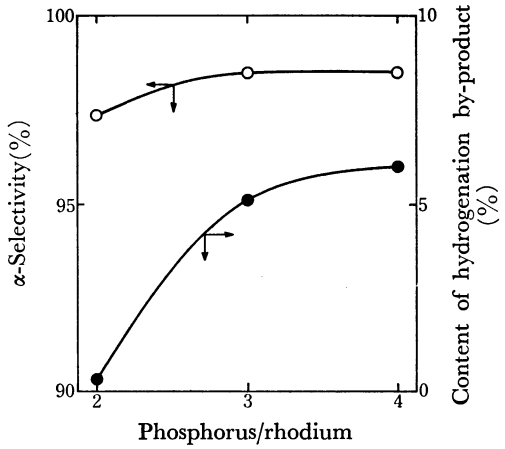


Fig. 1. Effects of the ratio of phosphorus/rhodium in hydroformylation of ethyl acrylate.
100 °C, 100 atm ($CO/H_2=1/1$), phosphine; $Ph_2P(CH_2)_4PPh_2$.

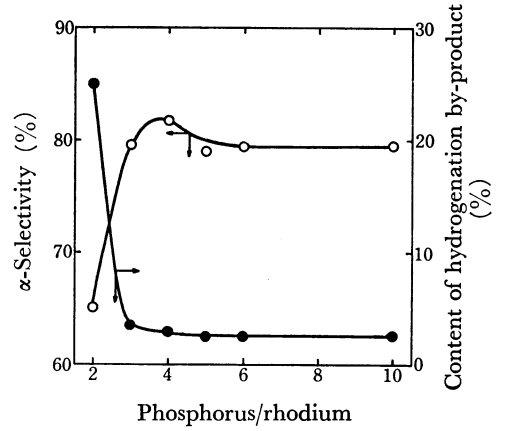


Fig. 2. Effects of the ratio of phosphorus/rhodium in hydroformylation of methyl methacrylate.
150 °C, 100 atm ($CO/H_2=1/1$), phosphine; $Ph_2P(CH_2)_2PPh_2$.

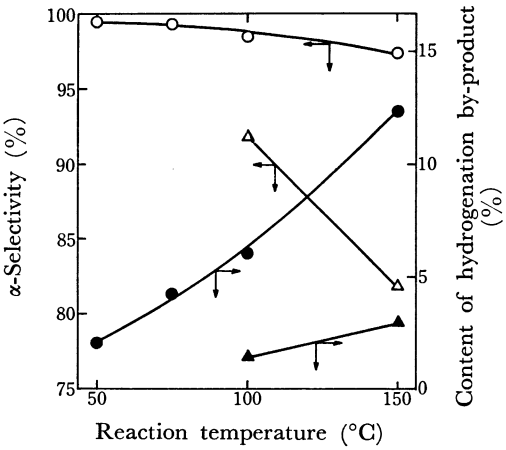


Fig. 3. Effects of the reaction temperature.
○,●: Ethyl acrylate: 100 atm ($CO/H_2=1/1$), phosphine; $Ph_2P(CH_2)_4PPh_2$, phosphorus/rhodium=4/1.
△,▲: Methyl methacrylate: 100 atm ($CO/H_2=1/1$), phosphine; $Ph_2P(CH_2)_2PPh_2$, phosphorus/rhodium=4/1.

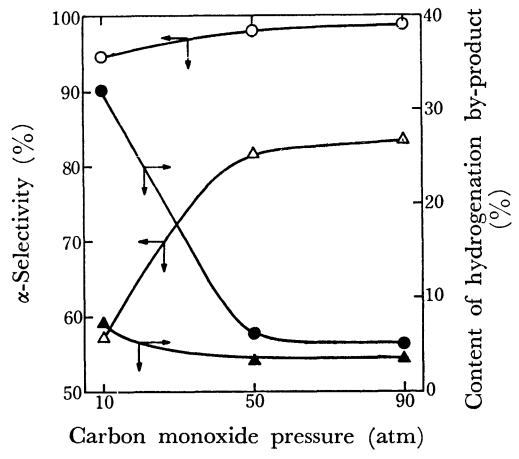


Fig. 4. Effects of the carbon monoxide pressure.
○,●: Ethyl acrylate: $p(H_2)=50$ atm, 100 °C, phosphine; $Ph_2P(CH_2)_4PPh_2$, phosphorus/rhodium=4/1.
△,▲: Methyl methacrylate: $p(H_2)=50$ atm, 150 °C, phosphine; $Ph_2P(CH_2)_2PPh_2$, phosphorus/rhodium=4/1.

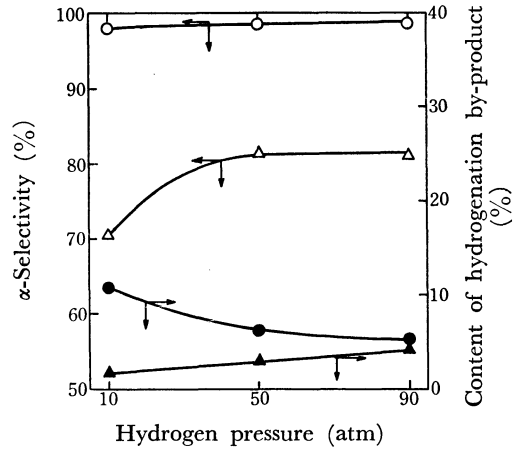


Fig. 5. Effects of the hydrogen pressure.
○,●: Ethyl acrylate: $p(CO)=50$ atm, 100 °C, phosphine; $Ph_2P(CH_2)_4PPh_2$, phosphorus/rhodium=4/1.
△,▲: Methyl methacrylate: $p(CO)=50$ atm, 150 °C, phosphine; $Ph_2P(CH_2)_2PPh_2$, phosphorus/rhodium=4/1.

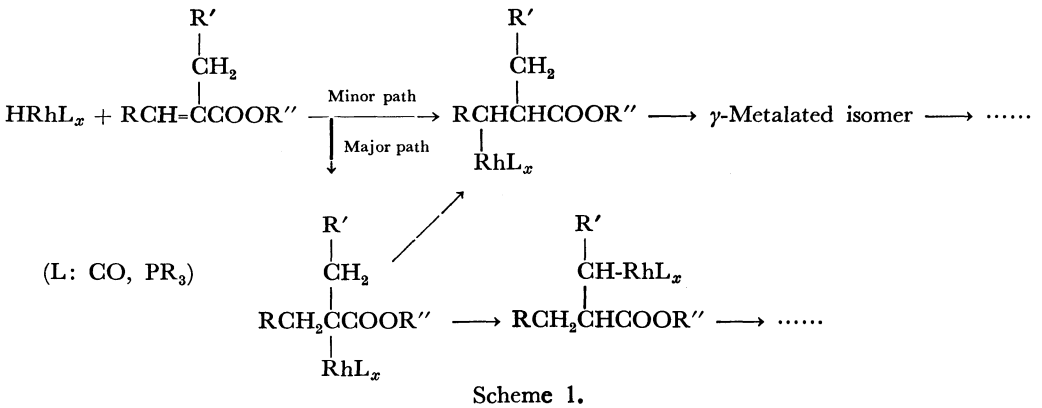
selectivity and decreased the extent of hydrogenation for ethyl acrylate as well as methyl methacrylate (Fig. 3); therefore, it provides a very favorable condition for selective α-formylation. For example, when ethyl acrylate was allowed to react with synthesis gas (100 atm, $CO/H_2=1/1$) at 100 or 75 °C by the use of 1,4-bis(diphenylphosphino)butane (phosphorus/rhodium=4/1), the reaction was completed within 12 or 65 min respectively, and ethyl α-formylpropionate was obtained in a 92.6 or 95.1% yield (98.5 or 99.3% α-selectivity) respectively.

For both the substrates, the α-selectivity and the amount of hydrogenation by-product increased and decreased respectively with an increase in the carbon monoxide pressure up to *ca.* 50 atm; thereafter it remained practically unchanged (Fig. 4).

As Fig. 5 shows, the effect of the hydrogen pressure on the α-selectivity was smaller than, but similar to, that of the carbon monoxide pressure for both ethyl acrylate and methyl methacrylate. On the other hand, concerning the hydrogenation by-product formation, acrylate and methacrylate behaved differently from each other on a variation in the hydrogen pressure. Thus, for acrylate, a higher pressure suppressed the competitive hydrogenation. The influence of the hydrogen pressure on methacrylate was the reverse.

Discussion

As has been described above, the rhodium–diphosphine system is a very beneficial catalyst for the selective α-formylation of α,β-unsaturated esters. As concerns the isomer distribution, Takegami and his co-workers[4] have examined the hydroformylation of ethyl acrylate catalyzed by rhodium carbonyl under various reaction conditions. On the basis of the results, they have suggested that the extent of the skeletal isomerization of the α-metalated intermediate, which is preferably formed initially, is an important factor in deciding the product distribution. With the present catalyst system, the effects of the reaction variables on the α-selectivity in the reaction of ethyl acrylate were qualitatively the same as the above authors had observed. In addition, γ- and/or β′-isomers were also produced in the reaction of crotonate and tiglate. These results seem to indicate that such an isomerization occurs also with the diphosphine–rhodium catalysts (Scheme 1). The α-selectivity for methyl methacrylate was more sensitive to the reaction conditions than for ethyl acrylate. This can also be reasonably explained from the point of view of the skeletal isomerization; *i.e.*, the possibility of the skeletal isomerization of the α-metalated intermediate from methacrylate is greater than that from acrylate, because the former has two carbons onto which the rhodium can migrate through isomerization, while the latter has only one such carbon. However, judging from the extremely high α-selectivity and its low sensitivity to the reaction conditions compared with those reported by Takegami *et al.*, it might be better to consider that the extent of the skeletal isomerization is not so great with the present catalyst system. The shorter carbon-chained (C_2–C_4) diphosphines may coordinate tightly to rhodium because of their chelating power, and may thus stabilize the α-metalated intermediate predominantly formed initially, retarding the possible skeletal isomerization prior to the CO insertion. This may be at least one of the reasons why the high α-selectivity is realized by the use of these shorter-chained diphosphines as additional ligands, though the possibility that the chelation of the diphosphines facilitates the CO insertion itself, considering the unexpected acceleration of the reaction of ethyl acrylate by the shorter-chained diphosphines, can not be ruled out. Such a retardation of skeletal isomerization due to the stabilization of the reaction intermediates caused by the addition of a phosphine to the reaction system is also observed in the palladium-catalyzed isomerization of straight-chained acyl halides to the corresponding branched-chained ones.[15]



Scheme 1.

On the other hand, the α-selectivity varied sensitively depending on the chain length of the diphosphine. Moreover, the effect of the chain length on the α-selectivity appeared in a different manner from substrate to substrate. These results indicate that the size and the conformation of the chelate ring have much to do with the α-selectivity and the reaction rate. Concerning the hydrogenation of olefinic compounds, Kagan and his co-workers[16] have reported that the catalytic activity of some diphosphine–rhodium complexes heavily depends on the combination of the diphosphine and the substrate.

In consideration of the effect of the size and the conformation of the chelate ring formed by α,ω-bis(diphenylphosphino)alkanes in the present reaction system, it may be reasonable to assume that any factors weakening the coordination of a diphosphine as a bidentate ligand are harmful to a high α-selectivity, because the addition of a diphosphine is essential for selective α-formylation. The chelate ring formed by the coordination of a diphosphine with a longer methylene chain linking the two diphenylphosphino groups should become progressively less stable as the rings become larger. Moreover, the so-called medium rings, such as the eight-membered ring formed by 1,5-bis(diphenylphosphino)pentane, suffer a further destabilization due to the transannular steric repulsion. Therefore, it is likely that the longer-chained diphosphine functions as a monodentate ligand with a free phosphorus end. The low α-selectivity observed with 1,5-bis(diphenylphosphino)pentane, which lies on a level with that with $Rh_2Cl_2(CO)_4$ alone or in the presence of triphenylphosphine, may be because of the above reasons.

The reaction with 1,3-bis(diphenylphosphino)propane also caused a relatively low α-selectivity, with the exception of the case of ethyl acrylate. This may be explained as follows: 1,3-bis(diphenylphosphino)propane forms a six-membered ring on chelating coordination, the ring being preferably of a chair form. As is well known in the cyclohexane chemistry, there arises a serious steric repulsion between 1,3-diaxial substituents of chair-formed cyclohexanes. Regarding the present six-membered ring containing a rhodium and two phosphorus atoms, a pair of phenyl groups bonded to the separate phosphorus atoms cannot help occupying the 1,3-diaxial position. This may weaken the coordination of the diphosphine and bring about the formation of some non-α-selective catalytic species in which the diphosphine does not effectively chelate the rhodium. The relatively lower α-selectivity for methyl methacrylate as well as for methyl crotonate with 1,3-bis(diphenylphosphino)propane than that with 1,2-bis(diphenylphosphino)ethane or 1,4-bis(diphenylphosphino)butane may be ascribable to the partial participation of these non-α-selective species. However, the above-mentioned tendency for this diphosphine to cause a lower α-selectivity did not appear explicitly in the case of ethyl acrylate. In consideration of this point, careful attention should be paid to the reaction rate: the reaction without any additional ligand or in the presence of triphenylphosphine proceeded very sluggishly. On the other hand, the reaction with the shorter diphosphines was extremely fast. Judging from this great difference in the reaction rate between these two cases, it may be reasonable to consider that the species in which 1,3-bis(diphenylphosphino)propane does not effectively chelate the rhodium can scarcely participate in the reaction to such a great extent as to influence the results, while the species with the chelating diphosphine effects a rapid and highly α-selective formylation. This may be the reason why a high α-selectivity was attained for ethyl acrylate even by the use of 1,3-bis(diphenylphosphino) propane.

As another factor playing an important role during the reaction, a steric interaction of the substrate with the catalyst should be taken into account. The introduction of a methyl group into the α-position of acrylate (methyl methacrylate) lowered the α-selectivity, probably because of the increased steric repulsion around the α-carbon to be preferentially metalated. However, unexpectedly, the introduction of a methyl group into the β-carbon (methyl crotonate) also lowered the α-selectivity. Moreover, 1,2-bis(5*H*-dibenzophospholyl)-ethane, in which the rotation of the phenyl groups around the phenyl-to-phosphorus-bond axis is inhibited by the connection of the two phenyl groups on each phosphorus atom to each other at the ortho position, caused a much poorer activity and a far lower α-selectivity in the hydroformylation of ethyl acrylate than the more flexible 1,2-bis(diphenylphosphino)ethane. These results suggest that a delicate steric interaction between the substituents of the catalyst ligands and those of the substrates should be taken into consideration. The steric requirement for the coordination of a substrate should be more severe as the steric bulk of both the substrate and the other ligands increases. This is

supported by the fact that the α-selectivity for methyl methacrylate and crotonate varied more sensitively with the structure of the catalyst than that for ethyl acrylate. However, the mode and the extent of this kind of steric interaction must be very dependent on the conformation of the ligand, and more precise knowledges about the real structure of the catalyst under the reaction conditions will be necessary in order to develop a more subtle argument.

Finally, concerning the electronic aspects, the authors did not find any direct and distinct evidence that the variation in the α-selectivity as well as in the reaction rate observed with various diphosphines, including such powerful electron donors as α,ω-bis(dicyclohexylphosphino)alkanes, was dependent on the electronic factor of the diphosphines. Probably, this is because the steric factors much more seriously affect the results.

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