A Bulky Phosphite-Modified Rhodium Catalyst for the Hydroformylation of Unsaturated Fatty Acid Esters

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ABSTRACT: A series of hydroformylation experiments was performed with a high-grade and a technical-grade-derived methyl oleate (MO) and a rhodium catalyst modified by the bulky tris(2-*tert*-butyl-4-methylphenyl)phosphite. In the hydroformylation of pure methyl oleate, relatively high turnover numbers were obtained (400–500 mol/mol/h) under mild conditions (molar ratio MO/Rh = 910, 80–100°C and 20 bar; CO/H_2 = 1:1, solvent toluene), leading to about 95% conversion in 3 h. Fast isomerization occurs under these conditions to produce the *trans* oleate. *Trans* oleate reacts more slowly than *cis* oleate. At temperatures below 50°C, isomerization does not occur. The use of technical-grade methyl oleate, containing 14% 9,12 diene, methyl linoleate (ML), results in lower reaction rates because dienes form stable π-allylic intermediates, which slowly undergo hydroformylation. More severe conditions were applied to obtain higher rates. The rate varied from 50 to 400 mol/mol/h, depending on conditions (molar ratio MO/Rh = 910, T = 50–120°C, P = 50–80 bar; CO/H_2 = 1:1–1:6, solvent, toluene). Several isomers of ML were formed during the reaction. Subsequent hydroformylation of these isomers results in a complicated mixture of products. The product mixture consists predominantly of methyl formylstearate, methyl formyloleate, methyl diformylstearate, and some yet unidentified side products. A comparison of the classic triphenylphosphine-modified catalyst and the bulky phosphite-modified catalyst has shown that the latter is several times more active.
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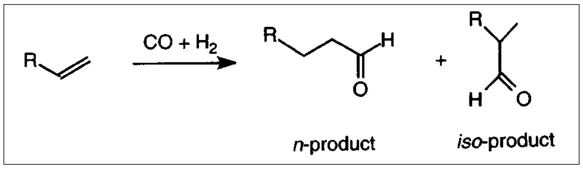
KEY WORDS: Bulky phosphite, fatty acid esters, hydroformylation, methyl oleate, rhodium.

Declining petroleum resources and environmental factors have resulted in a steadily increasing demand for renewable feedstocks derived from agricultural products for the chemical industry. Most agricultural products are not suitable for use in industry without introduction of new functional groups. Therefore, there is an ever-growing need for clean methods to introduce additional functionalities in natural products without formation of large amounts of chemical waste.

In the hydroformylation reaction, olefins react with synthesis gas to form aldehydes that contain an additional carbon atom. This reaction is a mild and clean procedure for functionalizing unsaturated compounds and is compatible with many other functional groups, such as esters, amides, and nitriles. The atom economy of the reaction is 100%, i.e., all atoms of the reactants end up in the product (1), which results in a minimum of chemical waste production (Scheme 1).

Several investigations have been performed on the hydroformylation of unsaturated fatty materials, such as oleic acid and methyl oleate (MO). Properties of the hydroformylation products vary, depending on the catalyst system and substrates used, and many areas of application for these oxo-products are known; e.g., lubricants (2), plasticizers (3–5), urethane foams (6–8), and coatings (9,10). Subsequent oxidation of the product aldehydes results in fatty diacid derivatives, which are important intermediates in the production of cosmetics. Hydroformylation of unsaturated fatty acid esters has been reported both with cobalt and rhodium catalysts, and several reviews concerning this topic have appeared (11–13). MO as well as various polyunsaturated fatty esters can be hydroformylated with cobalt carbonyl to mainly isomeric mixtures of mono formyl compounds (11,13–15). Double-bond isomerization, both geometric and positional, has been demonstrated to occur before hydroformylation. The product is a mixture of positional isomers. Several authors have described the formation of linear formylated products (14,16). With increasing temperature and in the presence of tributylphosphine, the proportion of the linear-chain compound increased.

In the late sixties, several novel hydroformylation catalysts were reported. These catalysts consisted of various substituted phosphine, phosphite, arsine and stibine ligands, used together with cobalt iridium or rhodium (17). These new catalysts were generally more active than cobalt carbonyl and



SCHEME 1

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promoted hydroformylation of olefins under milder conditions. Frankel (17) reported a highly selective rhodium system for the hydroformylation of MO into methyl 9(10)-formylstearate at relatively mild conditions (T = 100–110°C, *P* = 70–140 bar). The catalyst existed of rhodium, supported on C, $CaCO_3$, or Al_2O_3, and complexed with triphenylphosphine. Under hydroformylation conditions, the rhodium is solubilized in the reaction mixture to form a homogeneous rhodium carbonyl triphenylphosphine complex.

In 1983, van Leeuwen and Roobeek (18) reported new phosphite-based catalysts that showed high rates for otherwise unreactive (internal and branched) olefins. They received considerable follow-up in the open literature and in patent literature (19–38). Owing to their high reactivity, these bulky phosphite-modified catalysts may offer new possibilities for the development of a commercial process for the hydroformylation of fatty acid esters.

In our laboratory, we conducted exploratory investigations with a rhodium catalyst that was modified by the bulky tris-(2-*tert*-butyl-4-methylphenyl)phosphite in the hydroformylation of MO. The availability of pure oleate is limited. Therefore, it is more realistic to look at commercially available technical-grade oleates. These technical-grade oleates also contain other saturated and (multiple) unsaturated acid esters. In our experiments, we used a substrate obtained by vacuum distillation of a technical-grade oleate. After distillation, the substrate consisted of 84 mol% MO and 13.5 mol% methyl linoleate (ML). The remaining consisted of methyl stearate, methyl palmitate, and methyl palmitoleate.

EXPERIMENTAL PROCEDURES

$Rh(CO)_2acac$ was purchased from Degussa AG (Hanau, Germany) and used as received. MO (99% pure) was purchased from Aldrich chemie (Zwijndrecht, The Netherlands). The mixture of MO (86 mol%) and ML (14 mol%) was obtained by fractional distillation of technical-grade methyl oleate (Aldrich). Toluene was distilled from sodium/benzophenone. Syngas (CO 3.0/H_2 5.0 = 1:1), H_2 5.0, and CO 3.0 were purchased from Indugas Nederland BV (Vlaardingen, The Netherlands), and used as received. Tris-(2-*tert*-butyl-4-methylphenyl)phosphite was prepared according to a literature procedure (32).

^{1}H-nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AMX 300 instrument (Bruker Spectrospin N.V., Wormer, The Netherlands). Chemical shifts are given in ppm. Tetramethylsilane (TMS) was used as reference, with $CDCl_3$ as internal standard. Gas chromatography/mass spectrometry (GC/MS) was measured on a Hewlett-Packard 5890/5971-GC/MS (Hewlett Packard Nederland B.V., Amstelveen, The Netherlands). The GC was equipped with a J&W Scientific DB-5MS column (length 12 m, i.d. 0.20 mm, film thickness 0.33 μm) purchased from Interscience B.V. (Breda, The Netherlands). Composition was cross-linked phase 5% PhMeSiloxane, and the carrier gas was 70 kPa He.

Gas chromatographic analyses were run on a Carlo Erba HRGC 5300 mega series, purchased from Interscience, equipped with a flame ionization detector (FID), cold-on-column injection (injection volume 0.1 μL) on a J&W Scientific (Interscience) column DB1 (25 m, i.d. 0.53 mm, film thickness 0.15 μm) or an Interscience HRGC mega 2 series, provided with an FID and J&W Scientific (Interscience) column DB5 (30 m, i.d. 0.32 mm, film thickness 0.25 μm). The samples were filtered over neutral alumina and diluted with acetone to about 1 μmol of methyl esters per mL acetone (injection volume 0.1 μL).

The experiments were carried out in a 200-mL autoclave, equipped with sampling facilities, heating jacket, and magnetic stirrer. In all experiments, rhodium dicarbonylacetyl acetonate was used as catalyst precursor (added as a standard solution of $Rh(CO)_2acac$ in toluene, 4 mM). Before adding the substrate, it was filtered over neutral alumina to remove impurities, such as peroxides.

In a typical experiment, the autoclave was charged with 1 mL of the $Rh(CO)_2acac$ solution in toluene (4.10^{-3} mmol Rh), 52 mg (0.1 mmol) of the ligand, a solution of 1.2 mL of the substrate (3.64 mmol) in 7 mL toluene (filtered over neutral-alumina), 15 mL toluene, and 0.3 mL *n*-hexadecane as internal standard for GC analysis.

The autoclave was purged four times with syngas (5 bar), and pressurized (17 bar). Upon heating to 80°C the pressure increased to about 21 bar. As the reaction proceeded, the pressure decreased. The pressure decrease and the temperature were recorded. The expected total decrease of the pressure at 100% conversion of MO = 1.15 bar. The reaction was stopped when the pressure did not decrease anymore, or after 23 h. The reactions were followed in time by taking samples, which were analyzed by GC, GC/MS, or NMR.

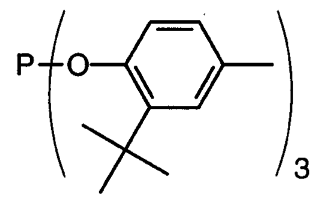
RESULTS AND DISCUSSION

In 1983, new phosphite-based catalysts were reported that showed fast rates for otherwise unreactive (internal and branched) olefins (18). These new bulky phosphites may offer higher turnovers at less severe reaction conditions for the hydroformylation of MO as compared to traditional hydroformylation with rhodium catalysts modified by triphenylphosphine and triphenyl phosphite (12,13,39).

Exploratory experiments were performed with the bulky tris-(2-*tert*-butyl-4-methylphenyl) phosphite as the modifying ligand in the hydroformylation of MO (Scheme 2).

The hydroformylation of unsaturated methyl esters can be accompanied by several side reactions, such as double-bond isomerization, *cis-trans* isomerization, and hydrogenation. This complicates product analysis considerably. The isomers formed are difficult to separate, and therefore, complete analysis of the products has not been attempted.

Hydroformylation of pure MO. A series of experiments was performed with high-grade MO (99% pure). These experiments were performed at mild conditions: 0.2 mM of Rh, phosphite/Rh = 25, substrate/Rh = 910, 80°C, and pressure of 20 bar synthesis gas (CO/H_2 = 1:1). The products were ana-



tris-(2-*tert*-butyl-4-methylphenyl)phosphite

SCHEME 2

lyzed by GC/MS and NMR. The reactions could also be followed by measuring the pressure decrease caused by consumption of CO and H_2 during the reaction. At the beginning of the reaction, the pressure decrease was relatively fast and became slower as the reaction proceeded. Based on the measured pressure drop, the conversion of MO was calculated to be about 85% in 2.5 h. It was expected that at least two isomers, methyl-9-formylstearate and methyl-10-formylstearate, were formed. No attempts were made to separate these products and other positional isomers of methyl formylstearate by GC.

The formation of the expected aldehyde products was confirmed by ^{1}H-NMR analysis. ^{1}H-NMR of the reaction products showed that a resonance signal had appeared at $\delta = 9.5$ ppm and that the resonance signal at $\delta = 5.3$ ppm (characteristic of the double-bond protons in MO) and the resonance signal at $\delta = 1.99$ ppm had disappeared almost completely. In methyl formylstearate, the ratio of aldehyde protons to methyl ester protons is 1:3. In the product sample, this ratio was 1:3.9. Therefore, we concluded that MO had not been converted completely. This quantitative analysis was confirmed by GC measurements.

The hydroformylation reaction was also performed at 100°C (Table 1, entry 2). The course of the reaction was followed in time by taking product samples periodically. GC analysis showed that, initially, a peak developed at a retention time beyond that of MO, while the relative height of the MO peak decreased. The mass spectrum of this compound is almost identical to that of MO. It appeared that this peak was the *trans* isomer of MO (methyl elaidate, ME) formed by *cis/trans* isomerization. This was confirmed with reference samples of ME. MO and ME were further hydroformylated to methyl formylstearate. Table 1 shows the time needed for conversion of 50% of the mixture of MO and ME. In other experiments, *cis/trans* isomerization of MO did not occur at 50°C. The GC diagram showed that some side products were formed (3.5%). The exact nature of these products has not been established. The time course of the reaction is shown in Figure 1.

In 2.5 h, the conversion of MO was about 90%, while at 80°C it was 85%. So, increasing of the reaction temperature from 80 to 100°C does affect the rate of the reaction only slightly. The cumulative turnover frequency of the reaction (TOF) initially increased, followed by a decrease. The turnover frequencies are calculated as the mean over the total reaction time. In this experiment, the catalyst precursor, the ligand, and the substrate were added at the same time. So, at the beginning of the reaction, the active catalyst still had to be formed, and consequently, TOF increased initially. In the literature, some examples are described of hydroformylation reactions of internal olefins with rhodium catalysts that were modified by bulky phosphites (18,29,31,32). These reactions are first-order in substrate concentration. It is assumed that, in correspondence with these reactions, hydroformylation of MO with the bulky phosphite-modified rhodium catalyst is also first-order in substrate concentration. The observed decrease of the rate of the reaction is explained by the decreasing concentration of substrate.

TABLE 1
Hydroformylation of Technical-Grade Methyl Oleate[a]

						Selectivity (%)				
Entry	L/Rh	T(°C)	P_{CO}	P_{H_2}	Time (h)[d]	MO	ME	ML	MFS	MFS (*iso*)
1[b]	25	100	10	10	1.2	11	39	0	49	1
2	25	100	10	10	6.8	5	37	6	43	2
3	25	120	10	10	4.7	5	37	3	45	3
4	25	50	40	40	3.3	32	10	5	44	1
5	25	80	40	40	1.6	16	26	5	45	1
6	25	100	25	25	2.0	10	32	5	44	1
7	25	100	10	60	1.2	11	32	2	43	2
8	25	100	40	40	1.9	6	36	5	42	0
9	5	80	40	40	5.3[e]	22	36	10	26	0
10	21.6	80	40	40	4.7	42	0	6	44	0
11[c]	6	80	40	40	1.6	0	50	0	50	0
12[c]	21	80	40	40	4.9	0	50	0	50	0

[a] See the Experimental Procedures section for conditions.
[b] Substrate: pure methyl oleate (MO).
[c] Substrate/pure methyl elaidate (ME).
[d] Reaction time required for 50% conversion of the sum of methyl oleate and methyl elaidate.
[e] Reaction time required for 30% conversion; ML, methyl linoleate; MFS, methyl formylstearate.

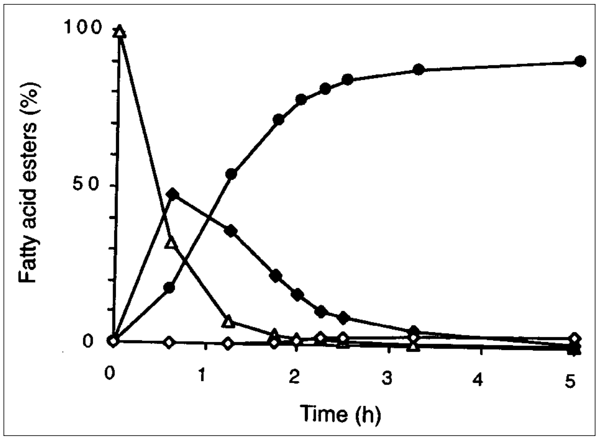


FIG. 1. Hydroformylation of pure methyl oleate (3.64 mmol). $P_{\text{initially}}$ = 20 bar, CO/H_2 = 1:1, T = 100°C, Rh = $4 \cdot 10^{-3}$ mmol, ligand/Rh = 25:1. △ Methyl oleate, ◆ methyl elaidate, ● methyl formylstearate, ◇ methyl formylstearate (isomers).

Hydroformylation of technical-grade MO. Because the availability of high-grade MO is limited, it is more realistic to use a technical-grade MO; this should give insight into the feasibility for the development of an industrially attractive process.

A series of experiments was performed with a technical-grade oleate. In these experiments, the reaction temperature and CO and H_2 pressure were varied. The substrate used was obtained by fractional distillation of a technical-grade oleate. This substrate consisted of 84% MO, 13.5% ML, 1.5% methyl stearate, and some methyl palmitate and methyl palmitoleate. The last two products were ignored in these experiments. The experiments were performed with standard quantities of catalyst precursor, ligand, and substrate. The reactions were followed by GC. The total amount of methyl esters in the first samples of each experiment was set to 100%. The amounts of methyl esters in the following samples were correlated to this amount by using the internal standard. The amount of methyl stearate in these samples was difficult to determine because methyl stearate has about the same retention time as an isomer of ML. From GC data of product samples, in which ML was hydroformylated almost completely, it seemed that the amount of methyl stearate did not change significantly during the reaction. Therefore, the amount of methyl stearate was set to 1.5% in the calculations.

Hydroformylation of ML with rhodium, modified by triphenylphosphine, is more difficult than that of MO, and more severe reaction conditions are required to obtain TOF of the same magnitude. ML binds more strongly to the catalyst, and the reaction rate is low because dienes form stable π-allylic intermediates which undergo hydroformylation slowly (40). Therefore, it is more difficult to hydroformylate MO in the presence of ML. The same holds true for the bulky-phosphite catalyst system used in these experiments.

The course of the hydroformylation reaction of technical-grade MO at 100°C is depicted in Figure 2. It took 6 h to reach 50% conversion of MO, while the pure MO needed 1 h (see Table 1). TOF values for the conversion of technical-grade MO are much lower than the TOF values for the pure substrate when the experiments are performed under the same conditions.

GC analysis of samples, taken just after addition of the substrate, and of product samples, taken during the reaction, showed that MO isomerized from *cis* to *trans,* and subsequently, the MO (*cis* and *trans*) was hydroformylated to methyl formylstearate. During the reaction, several new products appeared. GC/MS measurements showed that these products had a mass of 294 a.u. As the reaction proceeded, the height of these peaks decreased again. These observations led to the conclusion that ML isomerizes to a variety of compounds, which are subsequently hydroformylated. The individual isomers have not been analyzed. We concluded that there is competition between isomerization and hydroformylation. ML and its isomers are probably hydroformylated in two steps; methyl formyloleates are formed initially after one hydroformylation step. These products still contain one double bond that also can be hydroformylated, which results in diformylstearates.

At the higher temperature of 120°C, the reaction rate improved, but the trend of the reaction was the same (see Table, entry 3). At the beginning of the reaction, the formation of methyl formylstearate was slow. MO isomerized from the *cis* to the *trans* isomer, but it was hardly hydroformylated. Only after ML had disappeared, the formation of methyl formylstearate proceeded at a higher rate. This is also reflected in the TOF, which slowly increased with time, in contrast to the high initial reaction rates observed with pure MO as substrate (see Fig. 3).

Temperature dependence. The effect of the reaction temperature on the course of the reaction was studied at CO pressure

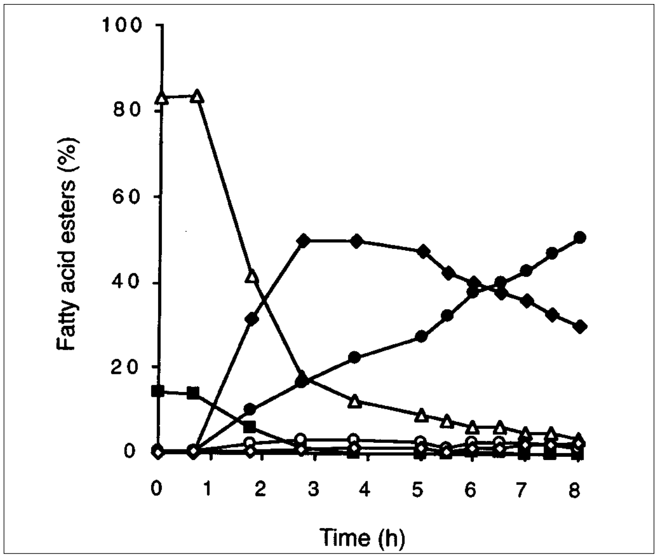


FIG. 2. Hydroformylation of technical-grade methyl oleate (3.64 mmol). $P_{\text{initially}}$ = 20 bar, CO/H_2 = 1:1, T = 100°C, Rh = $4 \cdot 10^{-3}$ mmol, ligand/Rh = 25:1. △ Methyl oleate, ◆ methyl elaidate, ■ methyl linoleate, ○ methyl linoleate (isomers), ● methyl formylstearate, methyl formylstearate (isomers).

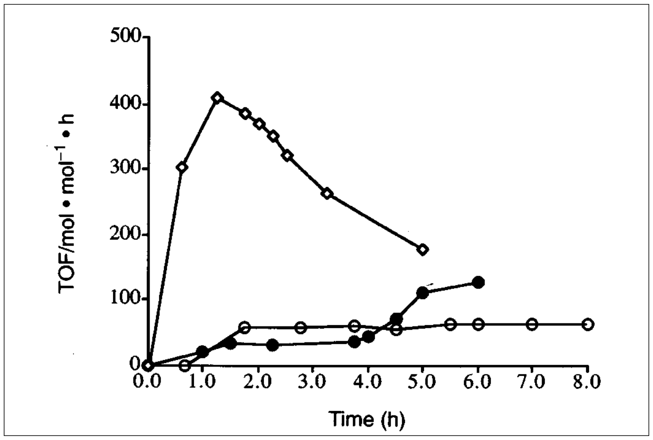


FIG. 3. TOF [mol/mol$_{rhodium}$/h] as a function of time for the hydroformylation of methyl oleate (3.64 mmol). $P_{initially}$ = 20 bar, CO/H_2 = 1:1, Rh = 4 · 10^{-3} mmol, ligand/Rh = 25:1. ◇ Pure methyl oleate, T = 100°C; ○ technical-grade methyl oleate, T = 100°C; ● technical-grade methyl oleate, T = 120°C.

and H_2 pressure of 40 bar. The decrease of the percentage of MO and ML with time was measured at 50 and 80°C (see Table 1, entries 4 and 5). The temperature dependence of the hydroformylation reactions was as expected, i.e., an increase of the reaction temperature resulted in a higher reaction rate.

Pressure dependence. The influence of CO and H_2 pressure on the rate of disappearance of MO and ML was investigated. These experiments were performed at 100°C. Table 1 shows that, at a higher initial pressure (CO/H_2 = 1:1), the rate of disappearance of MO is faster. The rate of disappearance of ML is almost equal at pressures of 50 and 80 bar (Table 1, entries 5 and 6), while at low pressure (20 bar, entry 2) it is slower. The rate law for hydroformylation of internal alkenes with bulky-phosphite ligands is known to have a negative order in CO concentration (32). The increase of the reaction rate at higher pressure is therefore assigned to the increased hydrogen pressure. At high pressure, the reaction rate does not increase any further, probably because of the retarding effect of the high CO partial pressure. The reaction rates could be further increased by using low CO pressure of 10 bar in combination with a high H_2 pressure of 60 bar (see Table 1, entry 7). As expected, the rates of disappearance of MO and ML increased with higher hydrogen partial pressure.

Substrate concentration. Because the hydroformylation of internal alkenes with bulky-phosphite ligands is known to be first-order in substrate concentration (32), an experiment was performed at higher substrate/rhodium ratio. At this higher substrate concentration, the rate of the hydroformylation reaction was increased. Both MO and ML were hydroformylated at a higher rate. The stability of the catalyst was not affected at this high substrate concentration. Even after 6 h, when the reaction was stopped, the catalyst was still active.

Triphenylphosphine as a ligand. Some experiments were performed with the traditional compound triphenylphosphine as the modifying ligand. The experiments were performed at ligand/rhodium ratios of 5:1 and 20:1. The results are shown in entries 9–12 (Table 1). At a ligand-to-rhodium ratio of 5, the extent of *cis-trans* isomerization of MO is considerable, while at the higher ligand-to-rhodium ratio, hardly any ME (MO-*trans*) is observed (Table 1, entries 9 and 10). Also, the rate of formation of methyl formylstearate is higher at this higher ligand-to-rhodium ratio. The higher rate of formation of methyl formylstearate can be explained by a combination of a reduced rate of isomerization of MO to ME and an increase of the rate of hydroformylation of MO. Alternatively, the rate of hydroformylation of ME might have been increased. The latter suggestion could be rejected on the basis of the observation made in hydroformylation experiments with ME as the substrate. These experiments were performed with triphenylphosphine as the modifying ligand at different ligand-to-rhodium ratios (Table 1, entries 11 and 12). From these experiments, it is clear that, at a ligand/rhodium ratio of 21, the rate of hydroformylation of ME is lower than that at a ligand/rhodium ratio of 6. The rate of hydroformylation of MO increases at a higher ligand/rhodium ratio (based on the first suggestion), while the rate of hydroformylation of ME decreases at a higher ligand/rhodium ratio.

Frankel (17) reported that the extent of double-bond migration is inversely proportional to the concentration of triphenylphosphine. In our experiments, the extent of *cis–trans* isomerization also seemed to be inversely proportional to the concentration of triphenylphosphine.

In Figure 4, the results obtained with the bulky-phosphite ligand are compared with the results obtained with triphenylphosphine as modifying ligand. The figure shows the decrease of the sum of the percentages of MO and ME of several experiments.

From these results we concluded that the bulky phosphite-modified catalyst has improved catalyst activity compared to the traditional triphenylphosphine-modified catalysts in hy-

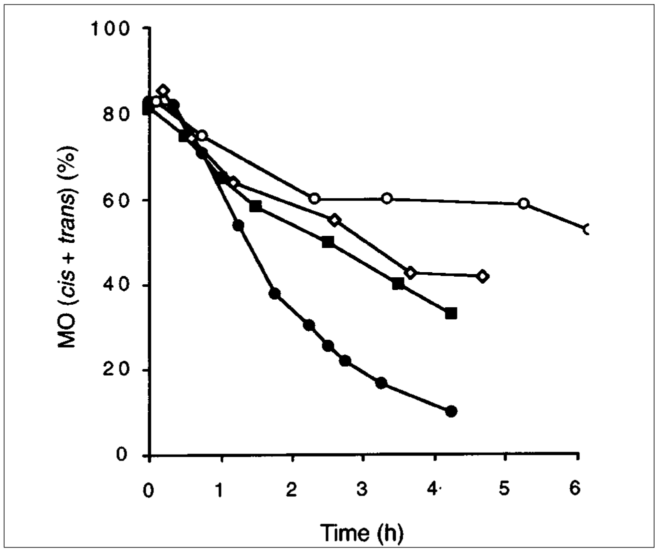


FIG. 4. Hydroformylation of technical-grade methyl oleate (3.64 mmol): bulky phosphite compared to triphenylphosphine as ligand. P = 80 bar, (CO/H_2 = 1:1), Rh = 4.10^{-3} mmol. ● Bulky phosphite, T = 80°C; ■ bulky phosphite T = 50°C; ◇ triphenylphosphine, L/Rh = 21.6, T = 80°C; ○ triphenylphosphine, L/Rh = 5.0, T = 80°C.

droformylation of technical-grade MO. Even at a temperature of 50°C, the bulky phosphite-modified catalyst is more active than the triphenylphosphine-modified catalyst at 80°C.

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