Journal of Organometallic Chemistry, 52 (1973) C55–C57
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

In situ high-pressure, high-temperature spectrophotometric studies of the chlorocarbonylbis(triphenylphosphine)rhodium(I) hydroformylation catalyst activated by hydroperoxides

H. BURNHAM TINKER* and DONALD E. MORRIS
Corporate Research Department, Monsanto Co., St. Louis, Missouri 63166 (U.S.A.)

(Received February 5th, 1973)

SUMMARY

The rate of hydroformylation of olefins catalyzed by $RhClCO(Ph_3P)_2$ (I) is accelerated by the addition of a small amount of cyclohexenyl hydroperoxide which converts I into *cis*-$RhCl(CO)_2Ph_3P$ (II), a very active olefin-hydroformylation and -isomerization catalyst.

The rates of olefin-hydrogenation[1,2,3] and -isomerization[4] by Group VIII metal phosphine complexes are accelerated by the presence of hydroperoxides and/or oxygen. We wish to report a similar rate enhancement observed during the hydroformylation of olefins catalyzed by $RhClCO(Ph_3P)_2$ (I).

A solution of purified cyclohexene* (0.20 mol) in *para*-xylene (130 ml) containing

TABLE 1

RATE OF THE HYDROFORMYLATION OF OLEFINS CATALYZED BY $RhClCO(Ph_3P)_2$ [a] AS A FUNCTION OF HYDROPEROXIDE PROMOTER

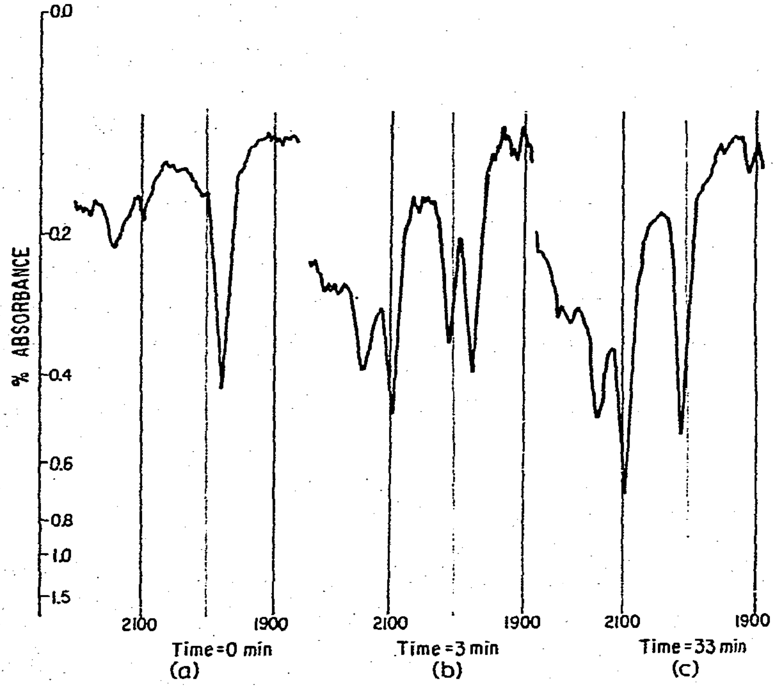
Olefin	*Hydroperoxide (mmol)*	*Ratio (Ph_3P/Rh)*	*Maximum rate of CO/H_2 consumption ($mol \cdot l^{-1} \cdot min^{-1}$) x 10^4*
cyclohexene	None	3 [b]	4.2
cyclohexene	2.1	3 [b]	180
cyclohexene	ABIN 0.1 g	2	5.0
1-hexene	None	3 [b]	235
1-hexene	2.1	3 [b]	420

[a] The concentration of rhodium complex was 5.0×10^{-3} *M* and of olefin was 1.5 *M*.
[b] Achieved by the addition of 0.75 mmol of Ph_3P.

---

*The purified olefins were distilled from $LiAlH_4$ immediately prior to use.

I (0.75 mmol) reacts with CO/H_2 (mole ratio 1 to 1, 33 atm) at 100° to give cyclohexanecarboxaldehyde at a very slow rate (Table 1). A similar solution containing cyclohexenyl hydroperoxide (2.1 mmol) reacts approximately 45 times as rapidly. The rate change follows an induction period and is accompanied by a change in the IR spectrum of the reacting solution (Fig. 1). These spectra were recorded during the natural progress of the reaction using a high-pressure, high-temperature spectrophotometer cell[5]. The initial spectrum (Fig. 1a) is that of the pure I (ν(CO) 1982 cm^{-1}); however, shortly after the addition of cyclohexene containing hydroperoxide, two new bands appear at 2093 and 2013 cm^{-1} (Fig. 1b and 1c). The intensities of the new bands increase as does the reaction rate until the 1982 cm^{-1} absorption completely disappears. The band at 2137 cm^{-1} is due to dissolved CO. Similar spectral changes are observed when 1-hexene containing cyclohexenyl hydroperoxide is hydroformylated; however, a rate acceleration of only 2 was observed. No spectral changes were observed in the absence of a hydroperoxide. The radical initiator α,α'-azodiisobutyronitrile had no effect on the rate of hydroformylation and the spectrum of the reacting solution.



Time=0 min (a) Time=3 min (b) Time=33 min (c)

Fig. 1. Infrared spectra of the reacting solution at various temperatures.

The rhodium complex, $[RhCl(CO)(Ph_3P)]_2$ (III) (ν(CO) 1992 cm^{-1}) was isolated from the reaction solution. In the presence of CO, III is rapidly converted to $RhCl(CO)_2Ph_3P$ (II) (ν(CO) 2093 and 2013 cm^{-1}). II is a novel, very active hydroformylation catalyst. We established the identity of II and III by elemental analysis, molecular weight determination, and by CO-evolution and -absorption measurements. The formulation of II and III were later confirmed by Galley *et al.*[6].

III is formed from I by the hydroperoxide oxidation of 1 mole of Ph_3P to Ph_3PO. However, neither II nor III contains Ph_3PO nor is it necessary for the rate acceleration observed. The direct synthesis of II via reaction 1 yields a catalyst identical to that

$$[RhCl(CO)_2]_2 + 2Ph_3P \rightarrow \underset{\text{(II)}}{2RhCl(CO)_2Ph_3P} \tag{1}$$

produced by the action of hydroperoxide on I determined by both *in situ* spectral and rate measurements. No induction period is observed.

The apparent absence of a large rate acceleration with 1-hexene is an artifact. Once formed, II catalyzes the rapid isomerization of 1-hexene to the internal isomers (detected by GLC analysis): The internal olefins undergo hydroformylation more slowly than the terminal hexene. Consequently, it is not possible to obtain the rate of hydroformylation of 1-hexene catalyzed by II for comparison with the rate catalyzed by I. The products of the hydroformylation of 1-hexene catalyzed by I are heptanal (74 mole %), 2-methylhexanal (26 mole %), and only a trace of 2-ethylpentanal. When II is employed as the catalyst the product distribution is substantially different (heptanal, 65 mole %; 2-methylhexanal, 30 mole %; and, 2-ethylpentanal, 5 mole %). The product distribution obtained when II is used as catalyst suggests that all hexene isomers undergo hydroformylation. Gas liquid chromatographic analysis shows that 1-hexene is not isomerized by I in the absence of cyclohexenyl hydroperoxide.

REFERENCES

1 H. van Bekkum, F. van Rantwijk and T. van de Putte, *Tetrahedron Lett.*, (1969) 1; H. van Rantwijk, Th.G. Spek and H. van Bekkum, *Rec. Trav. Chim. Pays Bas*, 91 (1972) 1057.
2 B.R. James and N.A. Memon, *Can. J. Chem.*, 46 (1968) 217.
3 R.L. Augustine and J.F. Van Peppan, *Chem. Commun,*, (1970) 495.
4 J.E. Lyons, *Chem. Commun.*, (1971) 562.
5 H.B. Tinker and D.E. Morris, *Rev. Sci. Instrum.*, 43 (1972) 1024.
6 J. Gallay, D. Demontauzon and R. Poilblanc, *J. Organometal. Chem.*, 38 (1972) 179.