HYDROFORMYLATION OF PROPENE CATALYZED WITH CARBONYLCHLOROBIS(TRIPHENYLPHOSPHINE)RHODIUM(I)

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Influence of some amines, amino acids, nitrogen heterocyclic compounds and urea derivatives (as ligands of carbonylchlorobis(triphenylphosphine)rhodium (*I*)) on velocity of the catalyzed hydroformylation of propene has been investigated. A positive effect on the catalytic activity has been found with the modifying ligands of very low basicity.

The hydroformylation of alkenes catalyzed with metal carbonyls[1,2] represents a widely used synthesis of aldehydes. Application of the catalysis modifiers reveals often new facts. *E.g.*, it was found[3,4] that a small addition of an amine accelerates the hydroformylation catalyzed with cobalt carbonyls. In a similar study[5] of the hydroformylation catalyzed with $[Rh(CO)_2Cl]_2$ in the presence of amines it was proved that the complexes $RhX(CO)_2L$ were formed in which X and L mean halogen and amine, respectively. Influence of $N(C_2H_5)_3$ was studied[6] in the case of the catalytic system $Rh(CO)Cl(PPh_3)_2$, and the found positive effect on the induction period was ascribed to its binding the hydrogen halide and facilitating the formation of hydride complex.

The present communication starts from our previous application studies[7], and it follows the effects of various nitrogen ligands of carbonylchlorobis(triphenylphosphine) rhodium(I) on velocity of the pressure hydroformylation of propene with synthesis gas (H_2 + CO mixture) under unified reaction conditions and on selectivity of the reaction for formation of C_4 aldehydes and ratio of butanal to methylpropanal.

The reaction time of 120 min was chosen for the catalyzed reaction in toluene solution; increase of the reaction time had no distinct effect on further consumption of the synthesis gas in most experiments (Table I). As the individual conversion curves differ in their course, we chose for the comparison parameter the time of consumption of 90% of total amount of synthesis gas.

The presence of strongly basic amines does not increase the reaction rate, and – on the contrary – it obviously facilitates side reactions which decrease the overall yields of the aldehyde and lead ultimately to formation of tarry products which make the catalyst regeneration difficult. Piperidine and decahydroquinoline cause rapid decomposition of the complex, due perhaps to hydrogenolysis of the ligand P–C bonds[8,9].

Application of the modifiers of very low basicity appears most favourable, but the activity of the system represents no simple function of the basicity order. Hence,

TABLE I

Effect of modifiers on hydroformylation of propene. τ time of reaching of 90% conversion of synthesis gas, α the propene conversion after 120 min, A percentage of the C_4 aldehydes in the product after 120 min, r butanal to methylpropanal ratio

Modifier	τ, min	α, %	A, %	r
Without any modifier	85	92	98	1·1
Diethylamine	80	96[a]	100[a]	1·2
Diphenylamine	55	96	100	1·2
Phenylcyclohexylamine	70	96	100	0·75
Triphenylamine	110	96	100	1·2
Tributylamine	80	100	53	1·5
Tribenzylamine	30	93	78	1·0
Aniline	45	98	82	0·75
2-Chloroaniline	80	100	100	1·1
N,N-Dimethylaniline	70	100[a]	100[a]	1·3
1-Naphthylamine	55	100[a]	100[a]	1·25
Triethylenediamine	80	93	67	0·9
Urea	35	100[b]	95[b]	1·2
N,N-Dimethylurea	22	100[b]	80[b]	1·3
Biuret	70	100	100	1·2
2-Cyanoacetamide	40	100	93	0·8
2,6-Diaminohexanoic acid	24	99[b]	96[b]	0·8
Glutamic acid	50	70	68	1·3
Aminoacetic acid	50	98	92	1·1
Pyridine	75	100	50	1·6
2-Methylpyridine	—	83	87	0·7
3-Methylpyridine	90	96[a]	84[a]	1·4
4-Methylpyridine	45	100	96	1·2
2,4-Dimethylpyridine	—	9	100	0·7
2,6-Dimethylpyridine	—	14	73	0·7
2,4,6,-Trimethylpyridine	—	11	91	0·7
Piperidine	100	84[c]	100[c]	1·1
Quinoline	25	100[b]	98[b]	1·1
cis-Decahydroquinoline	55	100	100	1·4
trans-Decahydroquinoline	45	100	100	1·5
1-Phenanthroline	—	51[c]	92[c]	1·7
Morpholine	65	100	98	1·1
N-Methylpyrrolidone	65	96	96	1·3

[a–c] Different time of the analyses (min): [a] 200, [b] 60, [c] 300.

the binding of hydrogen halide, presumed in earlier papers[6], has obviously no decisive effect on activity of the system, which is also supported by the results of experiments carried out in the presence of 2,6-diaminohexanoic acid. It is, however, possible to ascribe a stabilizing effect to the amine caused by its coordination, even though formation of stable complexes cannot be presumed. Whereas the complex $Rh(CO).H(PPh_3)_3$ is unstable in solution under normal pressure, an excess of amine increases substantially the stability of the hydride complex in similar way as the excess of phosphine. So, *e.g.*, addition of cyclohexylamine to solution of $Rh(CO)H(PPh_3)_3$ in chloroform causes a shift in $\nu(CO)$ from 1 922 to 1 932 cm^{-1}, the $\nu(RhH)$ being practically unchanged. Similarly, the ^1H NMR spectrum[10] shows a signal 20·05τ besides 19·8τ of the hydride hydrogen of $Rh(CO)H(PPh_3)_3$.

EXPERIMENTAL

The $Rh(CO)Cl(PPh_3)_2$ complex was prepared by the known method[8], $RhCl_3.3\,H_2O$ pure (Safina, Vestec), PPh_3 pure (Lachema), CO tech., toluene *p.a.* (Lachema), synthesis gas (46·6% v/v H_2, 52% CO, 1·1% N_2, maximum 0·3% O_2), propene pure (Slovnaft). All the used modifiers were of "pure" grade, 2,6-diaminohexanoic acid was used in the hydrochloride form.

The hydroformylations were carried out in 1 l stainless steel rocking autoclave. The modifiers (60 mol per 1 mol complex) were added to the standard starting mixture of 138 g 10^{-4}M solution of $Rh(CO)Cl(PPh_3)_2$ in toluene and 42 g propene (the complex to substrate molar ratio 10^{-4}). The autoclave was rinsed with synthesis gas whereupon its pressure was adjusted at 10^7 Pa at room temperature. The resistance heating enabled a rapid heating of the autoclave to the temperature of 100°C, and from this temperature being reached the pressure decrease was followed with time. After 120 min the product was analyzed: the C_4 aldehyde content and the butanal to methylpropanal ratio were determined chromatographically (a Mikrochrom 03 apparatus with a 250 cm × 3 mm column packed with 5% w/w Tridox on Chezasorb, hydrogen as the carrier gas), the propene conversion and content of aldehydic and alcoholic groups were determined also by modified oximation and acylation methods.

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