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HYDROFORMYLATION AND HYDROGENATION OF STYRENE WITH CARBON MONOXIDE AND WATER CATALYZED BY IRON CARBONYLS

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Summary

Styrene is hydrogenated to ethylbenzene and hydroformylated to 2- and 3-phenylpropanol by CO and H₂O in the presence of a Fe₃(CO)₁₂ + Et₃N + NaOH catalyst system at 140°C and 100 bar in H₂O/MeOH. The product composition depends strongly on the H₂O/MeOH ratio (A); alcohol formation is favoured at A = 3/1 and ethylbenzene formation at A = 1/2. 1,3-Diphenylbutane is formed as by-product.

Introduction

The synthesis of alcohols from olefins, carbon monoxide and water in the presence of iron carbonyls and a base was first described by Reppe in 1953 [1]. Later it was shown that aldehydes are the primary products of the reaction, and are then hydrogenated by the same catalyst system to the corresponding alcohols [2–5]. In most cases ethylene [1] or propylene [3–6] were used as olefins and information on the reactivity of higher olefins in this reaction is very limited. Single experiments have been described with cyclopentene [2], pentene-1 [7] and octene-1 [2] and the stoichiometric reaction between KHF₆(CO)₄ and styrene has been investigated [8].

Results and discussion

Styrene was chosen as the higher olefin to eliminate complications caused by olefin isomerization which may take place under the reaction conditions if aliphatic olefins are used [2]. Fe₃(CO)₁₂ was used as an iron carbonyl because of its ease of handling; it was recently shown [9] that under conditions very similar to those used in this work, Fe₃(CO)₁₂ and Fe(CO)₅ are equally effective as catalyst precursors.

TABLE 1

HYDROGENATION AND HYDROFORMYLATION OF STYRENE IN H₂O/MeOH (75/25 vv). EFFECT OF BASE COMPOSITION

Base (mmol)		Products (%)				
NaOH	Et ₃ N	Ethyl-benzene	Styrene	2-phenyl-propanol	3-phenyl-propanol	1,3-diphenyl-butane
0	10	29.7	69.5	0.7	0	0.1
2	8	37.3	42.5	16.6	2.4	1.2
4	6	33.7	48.3	15.0	2.0	1.0
6	4	24.0	48.8	21.9	3.8	1.5
8	2	9.5	78.8	9.5	1.8	0.4
10	0	9.9	82.7	2.5	0	4.9

The initial experiments, performed under conditions used for the Reppe-hydroformylation of ethylene and propylene (120–160°C, 50–200 bar CO, Et₃N as a base) were rather disappointing. Only very small amounts of ethylbenzene were formed and no hydroformylation products could be observed. Two additional variants were therefore included in the successive investigations: (a) the use of NaOH/Et₃N mixtures as base (which is effective in the reduction of acetone to isopropyl alcohol catalyzed by iron carbonyls under similar conditions [9]), and (b) the use of water/methanol mixtures as solvent (which results in significantly higher rates for the water gas shift reaction catalyzed by iron carbonyls under similar conditions [10]). The most significant results are shown in Tables 1–3 and Fig. 1.

TABLE 2

HYDROGENATION AND HYDROFORMYLATION OF STYRENE WITH NaOH/Et₃N = 4/6 BASE MIXTURE. EFFECT OF SOLVENT COMPOSITION

Solvent (%)		Products (%)				
H ₂ O	MeOH	Ethyl-benzene	Styrene	2-phenyl-propanol	3-phenyl-propanol	1,3-diphenyl-butane
0	100	14.7	81.1	0	0	4.2
9	91	30.1	61.2	0	0.0	8.7
25	75	76.1	18.1	0	0	5.8
39	61	79.8	14.2	0	0	6.0
50	50	67.7	28.0	0.3	0	4.0
60	40	59.6	21.3	14.6	1.1	3.4
67	33	22.8	62.0	10.4	0.2	4.6
70	30	18.0	50.5	28.4	1.2	1.9
75	25	32.1	45.0	18.4	2.5	2.0
78	22	9.7	62.3	24.8	1.6	1.6
80	20	18.5	53.8	24.0	1.2	2.5
84	16	16.5	70.4	10.0	0.1	3.0
90	10	17.1	67.7	12.2	1.8	1.2
100	0	1.9	98.1	0	0	0

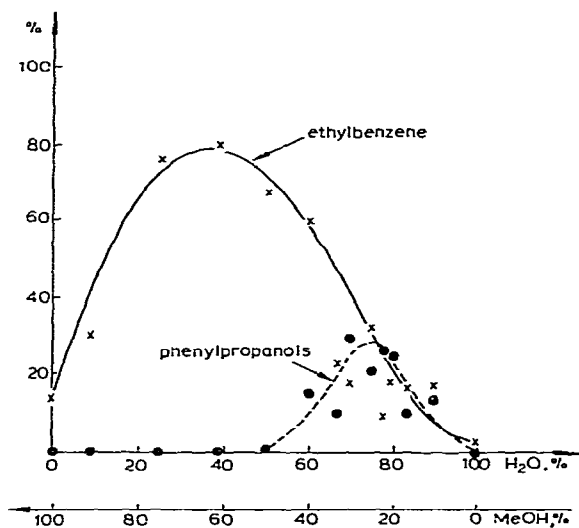


Fig. 1. Yields of ethylbenzene and phenylpropanol isomers (2-phenylpropanol + 3-phenylpropanol) in various H₂O/MeOH solvent mixtures. Base composition, NaOH/Et₃N = 4/6.

Optimum conditions for hydroformylation (coupled with the consecutive hydrogenation of aldehydes) were found to lie within a surprisingly narrow range around Et₃N/NaOH = 6/4 (Table 1) and H₂O/MeOH = 3/1 (Table 2 and Fig. 1). Although turnover numbers (mol alcohol/mol iron) do not exceed 3 even under such conditions and thus the activity of the catalyst is still low, the favourable effect of solvent and base composition is very marked, since under the usual conditions (water and Et₃N) practically no alcohol is observed. Taking account of the sensitivity of our gas chromatographic product analysis, this means that the rate of hydroformylation must have been increased by at least a factor of 100.

The rate of hydrogenation of styrene to ethylbenzene reaches its maximum at a different solvent composition, H₂O/MeOH = 1/2 (Fig. 1). The effect of

TABLE 3

HYDROGENATION AND HYDROFORMYLATION OF STYRENE IN H₂O/MeOH (25/75 vv). EFFECT OF BASE COMPOSITION

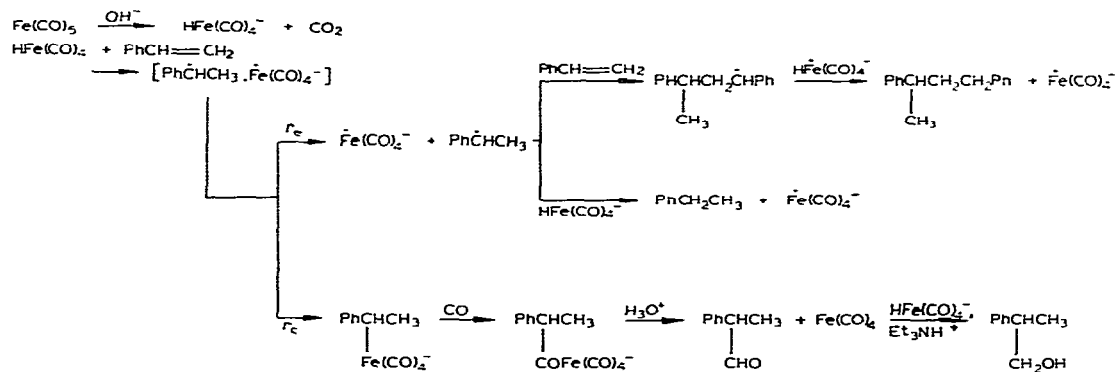
Base (mmol)		Products (%)				
NaOH	Et ₃ N	Ethylbenzene	Styrene	2-phenylpropanol	3-phenylpropanol	1,3-diphenylbutane
0	10	73.1	16.3	0	0	10.6
2	8	72.7	20.8	0	0	6.5
4	6	79.3	17.8	0	0	2.9
6	4	75.0	17.2	0	0	7.8
8	2	78.7	17.2	0	0	4.1
10	0	65.5	28.7	0.3	0	5.6

base composition is less marked, especially if a methanol-rich mixed solvent, which promotes hydrogenation, is used (Table 3).

The third product of the reaction is 1,3-diphenylbutane (identified by GC/MS). Its formation roughly parallels that of ethylbenzene but does not exceed 10%. Formally it can be regarded as the hydrogenated dimer of styrene, and to our knowledge no product of this type has previously been observed from olefin hydroformylation.

A few years ago Halpern demonstrated the formation of a radical pair intermediate in the stoichiometric hydrogenation of styrene with $\text{HMn}(\text{CO})_5$ [11]. Recently kinetic evidence was presented for a similar radical pair intermediate in the stoichiometric hydrogenation of styrene with $\text{HCo}(\text{CO})_4$ and the formation of $\text{PhCH}(\text{CH}_3)\text{COCO}(\text{CO})_4$ from styrene, $\text{HCo}(\text{CO})_4$ and CO [12]. On the basis of these analogies and the experimental results described above, we propose the sequences shown in Scheme 1 for the reactions of styrene under the conditions of Reppe-hydroformylation (Scheme 1).

SCHEME 1



The essential feature of Scheme 1 is the radical pair intermediate $[\text{Ph}\dot{\text{C}}\text{HCH}_3, \dot{\text{F}}\text{e}(\text{CO})_4^-]$. Its existence is supported by two experimental observations, (a) the formation of 1,3-diphenylbutane, and (b) the high branched/linear alcohol ratio (about 10/1), which is in strong contrast to the preferential formation of *n*-butanol from propylene with the same catalyst system [6].

Since according to this scheme hydroformylation and hydrogenation of styrene proceed through the same intermediate, their relative rates (and so the yields of alcohol and ethylbenzene) should depend on the ratio of the combination (r_c) and escape (r_e) reactions. The strong dependence on solvent composition of these two reactions looks surprising at first, but may be explained in terms of two opposing factors, viz. (a) increasing the amount of methanol in the solvent favours the reaction between styrene and $\text{HFe}(\text{CO})_4^-$, and thus the formation of the radical pair, by increasing the solubility of styrene in the polar phase, and (b) the probability of the combination reaction path (hydroformylation) increases with the "stability" of the solvent cage, which is probably greater the larger the number of strongly associating water molecules which surround the radical pair. As a result of these opposing factors, increase of methanol concentration will first increase the rate of both hydroformylation

and hydrogenation, but after a certain limit only favour the formation of free α -phenylethyl radicals and thus hydrogenation (and dimer formation). At very high methanol concentrations the amount of water may become insufficient, leading to a general fall in rate.

The Reppe-hydroformylation has now been found to be very solvent-sensitive. as may be expected for a reaction which proceeds in two non-miscible liquid phases and involves (among other things) the interaction of a charged and a neutral species. Other solvent combinations may prove to be even more favourable.

Experimental

A mixture of 10 mmol styrene (1.15 ml), 10 mmol of base (Et_3N and/or NaOH), 0.33 mmol of $\text{Fe}_3(\text{CO})_{12}$ (168 mg) and 5.4 ml of solvent (H_2O and/or MeOH) was placed in a 20 ml stainless steel autoclave, which was then flushed with Ar and pressured with CO to 100 bar. The autoclave was rocked for 3 h at 140°C . The product consisted of two phases which were separated. To the organic phase were added 5 ml of hexane and 1 g of solid NaOH , and the mixture was refluxed in air for 1 h to remove dissolved iron carbonyls. The resulting clear hexane solution was analyzed by GLC.

Identification of products by mass spectra:

2-phenylethanol, 136 (14) M^+ , base peak 105 (100) $\text{C}_6\text{H}_5\text{C}_2\text{H}_4^+$, 106 (28) $\text{C}_6\text{H}_5\text{C}_2\text{H}_5^+$, 91 (12) C_7H_7^+ .

3-phenylethanol, 136 (24) M^+ , base peak 117 (100) $\text{C}_6\text{H}_5\text{C}_3\text{H}_4^+$, 91 (97) C_7H_7^+ , 118 (76) $\text{C}_6\text{H}_5\text{C}_3\text{H}_5^+$, 92 (49) C_7H_8^+ .

1,3-diphenylbutane, 210 (22) M^+ , base peak 105 (100) $\text{C}_6\text{H}_5\text{C}_2\text{H}_4^+$, 91 (53) C_7H_7^+ , 106 (51) $\text{C}_6\text{H}_5\text{C}_2\text{H}_5^+$, 92 (46) C_7H_8^+ .

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