963. *The Hydroformylation of Propene.*

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In the hydroformylation of propene from 100 to 250° and from 250 to 2500 atm. the isomer distribution of the butyraldehyde products changes with temperature and pressure. Formation of n-butyraldehyde was favoured by low temperatures and high pressures. One explanation could be that the reaction proceeds through propylcobalt tetracarbonyl and propylcobalt tricarbonyl intermediates which are in equilibrium:

$$PrCo(CO)_4 \rightleftharpoons PrCo(CO)_3 + CO$$

PROPENE reacts with hydrogen and carbon monoxide under pressure and in the presence of dicobalt octacarbonyl to give n-butyraldehyde and isobutyraldehyde as products. This reaction is known as the OXO-synthesis or hydroformylation reaction. It is well established that at low temperatures n-butyraldehyde is formed in preference to isobutyraldehyde,[1,2] but the effect of the total pressure on the isomer distribution is not well understood. With very low partial pressures of carbon monoxide at low temperatures (90—

[1] Hughes and Kirshenbaum, *Ind. Eng. Chem.*, 1957, **49**, 1999.
[2] Macho, *Chem. prumysl*, 1962, **12**, 240.

110°) the proportion of n-butyraldehyde is markedly decreased.[3] We have studied the hydroformylation of propene from 100 to 250° and from 250 to 2500 atm. to obtain information on the influence and interaction of temperature and pressure on the butyraldehyde isomer distribution.

RESULTS

Hydroformylations were carried out in silver-lined equipment capable of withstanding 330° and 3000 atm. Equimolar quantities of hydrogen and carbon monoxide were used and measurements were made at temperatures from 100 to 250° and pressures from 250 to 2500 atm. The product was analysed quantitatively for n-butyraldehyde and isobutyraldehyde by gas chromatography after 65—75% conversion of propene. If the reaction was allowed to proceed to complete propene conversion the analysis was complicated by compounds formed by reactions of the products.[4] The yields of butyraldehydes from propene consumed were 94—98% for typical experiments. The product distribution was recorded as the percentage of n-butyraldehyde in the total butyraldehydes. The experiments were reproducible, and the product distribution was independent of catalyst concentration over the range of concentrations which could be experimentally explored. For example, in ten experiments at 160° and 1000 atm., using concentrations between 0·03 and 0·15 w/w % cobalt in heptane, the n-butyraldehyde (%) had an arithmetic mean of 76·7 with a standard deviation of 1·3. Below the given concentration range the reaction was very slow, and at concentrations above this the exothermic reaction proceeded so rapidly that the temperature increased uncontrollably. Thus, the study of catalyst concentration effects is limited by this experimental difficulty. When investigating the effect of pressure on the product distribution the temperature and catalyst concentration were held constant. The results are given in Tables 1 and 2, and Figs. 1 and 2.

DISCUSSION

Butyraldehyde Isomer Distribution.—At temperatures below 130° (Figs. 1 and 2) total pressure has little effect on the product distribution. However, at temperatures more usually associated with the hydroformylation process (130—200°) the total pressure has a marked influence, and this is most pronounced at 160° where the n-butyraldehyde increases from 56·5% at 250 atm. to 76·0% at 750 atm. It reaches a maximum at about 1000 atm. and then decreases slightly to 67—70% at 2500 atm. At 250° the proportion of n-butyraldehyde increases steadily with pressure up to 67—70% at 2500 atm. Thus, at low temperatures pressure is not very significant, whereas at high temperatures the formation of n-butyraldehyde is favoured by high pressures.

Mechanism.—It is suggested that hydroformylation of propene proceeds through two types of catalytic intermediate, one stable at low temperatures and high pressures, giving preferentially n-butyraldehyde, and another which exists in greater concentration at high temperatures and low pressures and gives a higher proportion of isobutyraldehyde.

TABLE 1.

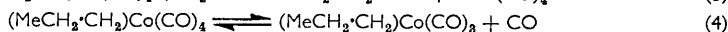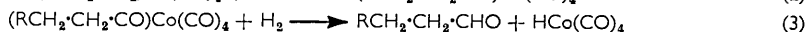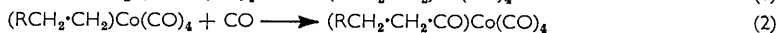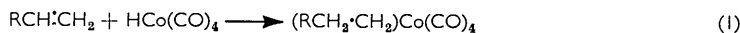Effect of temperature and pressure on product distribution.

Temp.	Co (w/w) % in heptane	n-Butyraldehyde (%) at pressures (atm.)							
		250	500	750	1000	1250	1500	2000	2500
100°	5·00	81·4	83·1	---	84·0	—	80·7	79·6	79·0
130	1·00	74·0 *	80·1	82·1	80·9 *	79·9	—	71·3	70·1
160	0·10	56·5 *	66·1 *	76·0	76·7 *	76·7	73·0	69·7	67·2
200	0·01	55·2 *	57·1	61·4	70·5 *	72·4	70·9	69·9	67·5
250	0·001	No reaction †	55·5 *	—	61·9 *	—	64·9	67·5	68·1

* Average of repeat experiments; see text concerning reproducibility. † Above 210° at 250 atm. no reaction occurs because of catalyst decomposition.

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[3] Pino, Piacenti, and Neggiani, *Chem. and Ind.*, 1961, 1400.
[4] Matsuda Akio and Uchida Hiroshi, *Tokio Kogyo Shikensho Makoku*, 1962, **57**, 50.

Recently, Breslow and Heck [5] suggested that hydroformylation proceeds through an alkyl-tetracarbonyl species, (1) ⟶ (3), or an alkyl-tricarbonyl species, $RCo(CO)_3$. Pino

$$RCH{:}CH_2 + HCo(CO)_4 \longrightarrow (RCH_2{\cdot}CH_2)Co(CO)_4 \qquad (1)$$

$$(RCH_2{\cdot}CH_2)Co(CO)_4 + CO \longrightarrow (RCH_2{\cdot}CH_2{\cdot}CO)Co(CO)_4 \qquad (2)$$

$$(RCH_2{\cdot}CH_2{\cdot}CO)Co(CO)_4 + H_2 \longrightarrow RCH_2{\cdot}CH_2{\cdot}CHO + HCo(CO)_4 \qquad (3)$$

$$(MeCH_2{\cdot}CH_2)Co(CO)_4 \rightleftharpoons (MeCH_2{\cdot}CH_2)Co(CO)_3 + CO \qquad (4)$$

et al.[3] postulated that both species were involved in the hydroformylation of propene, that they were in equilibrium (4), and that each species forms n-propyl- and isopropyl-cobalt carbonyls. They proposed that for steric and electronic reasons the propyl-tetracarbonyl

TABLE 2.

Comparison of effect of temperature on product distribution at 250 and 1000 atm.

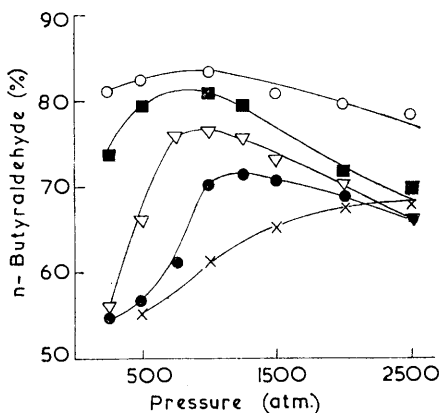| Temp.	Co (w/w) % in heptane	n-C_4H_8O (%) 250 atm.	n-C_4H_8O (%) 1000 atm.	Temp.	Co (w/w) % in heptane	n-C_4H_8O (%) 250 atm.	n-C_4H_8O (%) 1000 atm.
100°	5·00	81·4	84·0	160°	0·10	56·5 *	76·7 *
110	2·00	78·3 *	—	170	0·05	55·8 *	77·3
120	1·50	74·5 *	—	180	0·03	54·1 *	73·6
130	1·00	74·0 *	80·9	190	0·02	55·1 *	73·9
140	0·50	66·5 *	—	200	0·01	55·2 *	70·5 *
150	0·30	61·7 *	78·0	250	0·001	No reaction †	61·9 *

Refs. as in Table 1.

FIG. 1. Variation of the proportion of n-butyr-aldehyde produced with pressure at:
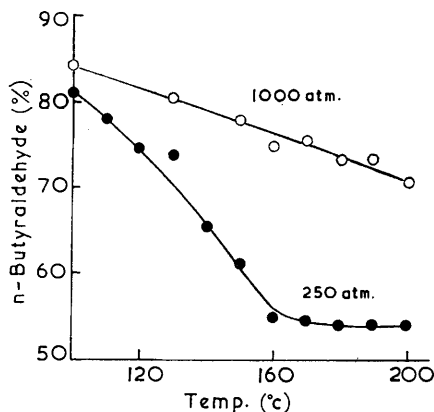
○, 100°; ■, 130°; ▽, 160°; ●, 200°; ×, 250°.

FIG. 2. Variation of the proportion of n-butyr-aldehyde produced with temperature, at 250 and 1000 atm.

species at equilibrium would be expected to contain more n-propyl isomer than the tricarbonyl, and thus the tetracarbonyl gives the higher proportion of n-butyraldehyde. This hypothesis is consistent with the present results between 250 and 1000 atm. High total pressure and low temperature would favour the tetracarbonyl species whereas low pressure and high temperature would favour the tricarbonyl species.

The step which determines the isomer distribution could occur at one or a combination of the following three stages of the reaction: direction of addition of the hydrocarbonyl [as (1)], isomerisation of the alkylcobalt carbonyls when formed, or isomerisation of the acylcobalt carbonyls. The butyraldehydes do not isomerise under hydroformylation conditions. Thus, before the hypothesis of Breslow and Heck and Pino *et al.* can be

[5] Breslow and Heck, *Chem. and Ind.*, 1960, 467; Heck and Breslow, *J. Amer. Chem. Soc.*, 1961, **83**, 4023.

accepted or developed the contribution of each stage of the reaction towards isomerisation must be determined.

The slight decrease in the percentage of n-butyraldehyde above 1000 atm. may involve a compressibility factor, forcing the propylcobalt tetracarbonyl equilibrium towards the isopropylcobalt tetracarbonyl. This follows if it is assumed that the molar volume of the isopropyl- is less than that of the n-propyl-tetracarbonyl, as an increase in pressure would drive the isomerisation equilibrium towards the isopropyl species,[6] thus giving more iso-butyraldehyde.

<center>EXPERIMENTAL</center>

The propene used contained 99·7% of propene and 0·3% of propane. Equimolar mixtures of carbon monoxide and hydrogen were employed throughout. Dicobalt octacarbonyl was used as catalyst at temperatures below 140° but at higher temperatures the cobalt carbonyl was formed conveniently *in situ* from cobalt nonanoate.

Typical Hydroformylation Experiment.—Cobalt nonanoate (0·1 g.) in heptane (13·5 g.) was placed in a silver-lined autoclave (100 ml.), fitted with a stirrer, which was connected to a compressor containing an equimolar mixture of carbon monoxide and hydrogen. The autoclave was cooled in ice, and evacuated, propene (23 g.) admitted, the system sealed, and the total pressure increased to 750 atm. The autoclave was heated by an electric induction heater to $160 \pm 2°$ in 8 min.; the pressure was adjusted to 1000 ± 50 atm. and maintained there throughout the reaction, and the reaction followed by measuring the uptake of gas. After 45 min., corresponding to 68% propene conversion, the vessel was cooled to room temperature with compressed air (10 min.). The product contained n-butyraldehyde (20·4 g.) and isobutyraldehyde (6·4 g.). Thus, 76·1% of the total butyraldehydes was the n-isomer.

The aldehydes were identified by infrared spectroscopy after separation by gas chromatography on a column packed partly with squalane on Celite and partly with 2,4-dinitrophenylhydrazine on Celite.

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[6] Hamann, "High Pressure Physics and Chemistry, Part 2," ed. Bradley, Academic Press. London and New York, 1963, ch. 7.