The Preparation of Dimer Aldehydes and Dimer Alcohols in an Oxo Reactor. I. Modifiers Effective in Producing Dimer Aldehydes and the Hydrogenation of the Aldehydes with Synthesis Gas

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The oxo process has here been modified to produce aldehydes with $2n+2$ carbon atoms in an oxo reactor, starting with an olefin of n carbon atoms. The modified oxo process was previously reported to use zinc metal and such zinc compounds as naphthenate and acetylacetonate as the modifiers,$^{1-3)}$ together with a cobalt carbonyl catalyst. However, previous work$^{4)}$ in our own laboratory has established that the hydroformylation rate is considerably decreased in the presence of zinc, presumably owing to the formation of an oil-soluble mixed carbonyl of $[Co(CO)_4]_2Zn$. The mixed carbonyl had already been discovered by Hieber and Schulten.$^{5)}$ The present paper deals first with search for more efficient modifiers and then with another attempt to obtain alcohols from the corresponding aldehydes by hydrogenation with the synthesis gas at the pressure prevalent in the oxo reaction conditions without removal of the cobalt carbonyl. Although the hydrogenation process using synthesis gas has been known for a long time,$^{6)}$ hydrogenation at a reasonable rate could be achieved only with difficulty under the pressure of the oxo reaction.$^{7)}$

Experimental

The synthesis run was conducted in a 300 cc. stainless-steel autoclave. The autoclave was connected by a copper tube and a needle valve to a pressure vessel (0.5 l. in volume) into which an equimolecular mixture of hydrogen and carbon monoxide had been compressed at the pressure of a little above 200 kg./cm^2. It was equipped with a stirrer with a vertical movement. A solution containing dicobalt octacarbonyl crystals, a solvent, and a modifier were placed in the autoclave. After

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1) P. A. Lobo, A. T. Ashton, D. C. Clidon and L. N. Vernon, *Chem. Eng.*, **1961**, Dec. 11, p. 70.

2) R. B. Mason, U. S. Pat. 2811567 (1957).

3) C. L. Aldridge et al., U. S. Pat. 2942034 (1960).

4) K. Bando, unpublished.

5) H. Hieber and H. Schulten, *Z. anorg. u. allgem. Chem.*, **243**, 145 (1939).

6) M. Orchin, "Advances in Catalysis," Vol. V, Academic Press Inc., N. Y. (1953), p. 385.

7) J. Berty, E. Olbad and L. Markó, *Chem. Tech.*, **5**, 283 (1957).

flushing the air out with the synthesis gas, the autoclave was loaded with some propylene and pressured with the synthesis gas from the pressure vessel to about 140 kg./cm^2 at room temperature; then the autoclave was heated. It took about 20 min. to heat the autoclave to 150°C. Thereafter, the stirring mechanism was started. During the reaction period, the temperature was controlled at 150 ± 1°C, and the pressure in the autoclave was maintained at 200 kg./cm^2 by the continuous introduction of the synthesis gas from the pressure vessel through the needle valve. Pressure falls in the pressure vessel with time were recorded. The amounts of synthesis gas calculable from the pressure falls stood for the gas consumption in the hydroformylation. After the reaction period of an hour or two hours, the autoclave was cooled in running water and the gas was purged and metered while the liquid product was weighed. In several cases, the gas was analyzed for unreacted propylene. The composition of the liquid product was determined gas chromatographically by means of a 3 m. column of cellite plus P. E. G. 1500, while the unreacted propylene was measured by means of a 2 m. column of alumina plus silicon oil.

The propylene was 93 mol.% pure and contained 6.5 mol.% propane and 0.5 mol.% ethane according to the gas chromatographic analysis. Solvents such as cyclohexane and *n*-butyraldehyde, which were free from any impurities detectable from gas chromatographic analyses, were obtained by the fractional distillation of the commercial products. Dicobalt octacarbonyl was manufactured by the reaction between cobalt carbonate in benzene and the synthesis gas at high pressure. The liquid content after the reaction was cooled to deposit crystals of the carbonyl, which were then stored for use in a pressure vessel under carbon monoxide.

A variety of the modifiers were examined for their effects on both the dimerization of aldehydes and the rate of hydroformylation. Among these, magnesium methylate, isopropylates of aluminum and titanium, and zinc naphthenate were from commercial sources; all of them except the last were supplied by the Kawakami Institute, Inc. The zinc isopropylate was prepared from zinc chloride and sodium isopropylate, while the zinc acetylacetonate was prepared from zinc carbonate and acetylacetone. The acetylacetonates of vanadium ($VO(C_5H_7O_2)_2$), chromium ($Cr(C_5H_7O_2)_3$), molybdenum ($MoO_3(C_5H_7O_2)_2$), and zirconium ($Zr(C_5H_7O_2)_4\cdot10H_2O$) were prepared, according to the method described in the literature,[8] by reacting acetylacetone with vanadium pentoxide, with chromium trichloride in the presence of urea, with molybdenum trioxide, and with zirconium oxychloride ($ZrOCl_2\cdot8H_2O$) in the presence of sodium carbonate respectively. The acetylacetonate of magnesium was the product obtained by the reaction between magnesium foil and acetylacetone, while that of titanium was prepared from titanium isopropylate and acetylacetone. Stannous oleate was prepared by the extraction with ether of a mixture of aqueous sodium oleate and aqueous stannous chloride, followed by the evaporation of the ether. In the experimental runs to study the hydrogenation of dimer aldehydes with the synthesis gas, the carbonyl of iron, besides that of cobalt, was used. It was prepared in a way which has been described elsewhere.[9]

Results and Discussion

The Effects of Modifiers on the Hydroformylation Rate and on the Yield of Dimer Aldehydes. — On the reasonable assumption[10] that the initial rate of hydroformylation is of the first order with respect to propylene concentration, the magnitude of an initial rate constant, k, evaluated by the aid of the formula $k=(1/t)\ln[c_0/(c_0-V/2)]$, where t is the reaction time (min.), c_0 is the initial amount of propylene (mole), and V is the amount of the consumed synthesis gas (mole) as estimated as mentioned afore,[11] gives an appoximate measure of the initial rate. In the present study, k is conventionally calculated by putting the value of t as the point at which $c_0-V/2$ is equal to $0.9\,c_0$.

Tables I and II summarize the results of experimental runs made to examine the effects of modifiers. The reaction conditions differ in some respects between series I of Table I and series II of Table II. The main difference is that in the former series cyclohexane was used as the reaction medium, while *n*-butyraldehyde was used in the latter series. Accordingly, the effects of modifiers can not be compared directly throughout the runs of the two series. However, an approximate and reasonable comparison is possible if the data with no modifiers in each of the series and the data with the modifiers (magnesium methylate and aluminum isopropylate) that are common to both the series are taken into consideration.

The choice of *n*-butyraldehyde as the reaction medium in series II was made after a few preliminary experiments, according to which a larger content of the dimer aldehydes in the product, as well as a higher rate of hydroformylation, was obtained by its use.[12] Moreover, the choice is preferable in view of the fact that in the industrial oxo reactor for aldehyde production from propylene, the

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[8] "Inorganic Synthesis," II, (1946) p. 121; V, (1957) p. 115, 130; VI, (1960) p. 147.

[9] H. Uchida, *Rpt. Gn't. Chem. Ind. Research Inst. Tokyo*, **44**, 43 (1949).

[10] A. R. Martin, *Chem. & Ind.*, **1954**, 1536.

[11] For a more rigorous estimation of V, the change of the partial pressure of propylene in the gas phase of the autoclave should be taken into account, since the partial pressure decreases with the progress of the hydroformylation.

[12] The experimental data will be reported elsewhere in detail.

hydroformylation proceeds in the medium of butyraldehydes.

In the tables, the conversion is calculated on the basis of the amount of synthesis gas consumed, or more accurately, of the amount of propylene unconverted. Data of the former calculation are shown in brackets. The product composition in Table I shows the composition of liquid product exclusive of cyclohexane, while that in Table II shows the composition of the total liquid product. The residue stands for matter not yet identified.

Although a comparatively small amount of zinc compound causes an increase in the yield of dimer aldehydes without much reduction of the rate of hydroformylation, a greater amount completely inhibits the progress of the reaction. The inhibition is similarly observed with zirconium acetylacetonate and stannous oleate. The acetylacetonates of titanium and vanadium considerably increased the yield of dimer aldehydes, with some decrease in the rate. Aluminum isopropylate and the acetylacetonates of chromium and molybdenum have scarcely any effect upon either the dimerization or the rate. In contrast to the above modifiers, magnesium compounds such as methylate and acetylacetonate appear to be significant in effectively increasing the yield of dimer aldehydes without any reduction of the hydroformylation rate. The investigation will hereafter be conducted by emphasizing the magnesium compounds.

The Dimerization Rate of *n*-Butyraldehyde in the Presence of Magnesium Methylate. — In order to obtain more comprehensive knowledge on the effect of magnesium methylate, the rates of the dimerization of *n*-butyraldehyde at the pressure and the temperature of the oxo reaction were measured in the presence of either dicobalt octacarbonyl or magnesium methylate, and then in the presence of both of them. The measurement was conducted by means of the determination of the contents of C-4 and C-8 aldehydes in several liquid samples (1 cc.) withdrawn from the initial charge of *n*-butyraldehyde (20 cc.) by means of a dip tube at time intervals over the dimerization period. The results are shown in Fig. 1 as plots of the respective aldehyde contents vs. the reaction time. The figure also includes the plots of the residue. The dimerization takes place in the presence of dicobalt octacarbonyl alone (curve I); the extent of this dimerization is rather high compared with that due to the presence of magnesium methylate alone (curve II). In their simultaneous presence (curve III), the extent is considerably increased, and the C-8 aldehydes are produced in an amount greater than the sum of the respective amounts of curves I and II.[13)]

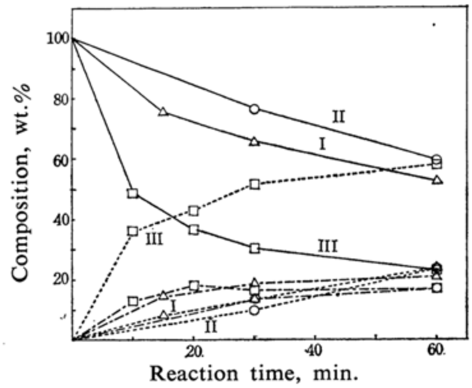

Fig. 1. Dimerization of *n*-butyraldehyde under high pressure of the 1 : 1 synthesis gas.
Reaction temperature, 150°C; the synthesis gas pressure, 200 kg./cm^2. Full line, *n*-butyraldehyde: dotted line, C-8 aldehydes; dotted and dashed line, residue.
-△- In the presence of 0.8 mmol. $Co_2(CO)_8$
-○- In the presence of 0.8 mmol. $Mg(OCH_3)_2$
-□- In the presence of 0.8 mmol. $Co_2(CO)_8$ plus 0.8 mmol. $Mg(OCH_3)_2$

The Effects of Organic Bases on the Hydroformylation Rate and on the Yield of Dimer Aldehydes. — It had already been established that the rate of hydroformylation is increased by the addition of small amounts of organic bases.[14)] With the intention of increasing the rate, the reaction was now carried out in the presence of one of the two organic bases, either pyridine or *N, N*-dimethylaniline, in addition to dicobalt octacarbonyl and magnesium methylate. The results are listed in Table III, which also includes the product composition after hydrogenation in the usual way, using a cobalt catalyst. Pyridine unexpectedly caused an increase in the yield of dimer aldehydes with an approximately equal rate, while *N, N*-dimethylaniline caused an increase in the rate with an invariable yield. The remarkable effect of pyridine can be seen more readily with the composition of the product after hydrogenation (cf. numerals in brackets).

The Direct Synthesis of C-8 Alcohols from Propylene in the Oxo Reactor. — As is recognizable in the foregoing tables, the products of hydroformylation at 150°C always contain

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13) As for the C-8 aldehydes in the products along curve II, only unsaturated ones are present, whereas in the products along curves I and III, the saturated ones are increasingly present with the passage of reaction time. The product of curve III after the reaction period of an hour contains a greater amount of the saturated C-8 aldehydes than of the unsaturated ones. Detailed data on the produt composition will be reported elsewhere.

14) I. Wender, H. W. Sternberg and M. Orchin, "Catalysis," Vol. V, Reinhold Publ. Corp., New York (1957), p. 109.

TABLE I. EFFECTS OF MODIFIERS ON HYDROFORMYLATION RATE AND YIELD OF DIMER ALDEHYDES (Series I)

Exp. No.	$Co_2(CO)_8$ mmol.	Modifier mmol.	Conversion %	k 10^{-2} min^{-1}	Product composition, wt.%						
					n-C_3H_7CHO	i-C_3H_7CHO	n-C_4H_9OH	i-C_4H_9OH	$C_7H_{13}CHO$	$C_7H_{15}CHO$	Residue
1	0.27	None	(80)	1.5	50.9	27.5	0.9	0.4	1.5	1.9	16.9
2	0.27	Zn naphthenate 0.53	(40)	0.4	26.2	28.6	3.5	1.6	13.1	13.5	13.5
3	0.27	Zn isopropylate 0.53	(50)	0.5	32.0	26.0	1.7	1.5	11.4	14.0	13.4
4	0.27	Al isopropylate 1.07	(80)	1.5	49.8	24.9	2.3	1.4	1.2	3.9	16.5
5	0.40	None	(100)	2.5	47.5	23.4	2.6	1.1	3.5	5.6	16.3
6	0.40	Mg methylate 0.85	99.5	2.6	30.8	26.6	2.1	1.1	3.7	21.9	13.8
7	0.50	Mg methylate 1.07	(100)	3.4	28.7	27.1	3.1	2.2	3.5	21.7	13.7
8	0.53	Ti isopropylate 1.07	(70)	1.3	25.7	24.6	4.6	2.3	4.3	22.1	16.4

The reaction conditions were as follows: The pressure was 200 kg./cm², the temperature was 150±1°C, and the reaction period was 2 hr. The initial charge included 0.2±0.01 mol. C_3H_6 and 0.056 mol. C_6H_{12}, besides $Co_2(CO)_8$ and modifiers.

TABLE II. EFFECTS OF MODIFIERS ON HYDROFORMYLATION RATE AND YIELD OF DIMER ALDEHYDES (Series II)

Exp. No.	Modifier[a]	Conversion %	k 10^{-2} min^{-1}	Product composition, wt.%						
				n-C_3H_7CHO	i-C_3H_7CHO	n-C_4H_9OH	i-C_4H_9OH	$C_7H_{13}CHO$	$C_7H_{15}CHO$	Residue
9	None	(98)	5.6	48.0	19.6	3.7	0.9	0.7	9.4	17.7
10	Al isopropylate	97.0	5.5	46.4	19.3	2.9	1.0	1.1	8.7	20.5
11	Mg methylate	(99)	5.8	35.6	19.2	3.1	1.1	3.1	22.6	15.4
12	Mg acetylacetonate	98.5	5.8	38.4	19.7	3.2	1.0	3.8	17.2	16.6
13	Ti acetylacetonate	93.2	3.3	35.8	18.5	3.5	1.4	6.9	13.4	20.5
14	V acetylacetonate	(94)	3.6	34.4	19.5	3.5	1.0	1.1	17.8	22.7
15	Cr acetylacetonate	(94)	4.5	47.3	21.2	3.2	1.7	1.6	9.2	15.8
16	Mo acetylacetonate	95.0	4.4	45.8	18.8	2.1	1.3	1.0	6.3	24.7
17	Zn acetylacetonate	0	0	—	—	—	—	—	—	—
18	Zr acetylacetonate	0	0	—	—	—	—	—	—	—
19	Sn oleate	0	0	—	—	—	—	—	—	—

a) The amount of modifiers was 0.8 mmol. throughout the runs. The reaction was carried out in the same way as in series I except that 0.068 mol. of n-C_3H_7CHO was used in place of cyclohexane and the reaction duration was an hour.

TABLE III. EFFECTS OF ADDITIONS OF ORGANIC BASES

Exp. No.	Organic base mmol.	Conversion %	k 10^{-2} min^{-1}	Product composion, wt.%[a)]								
				n-C_3H_7CHO	i-C_3H_7CHO	n-C_4H_9OH	i-C_4H_9OH	$C_7H_{13}CHO$	$C_7H_{15}CHO$	2-Ethyl-4-methylpentanol	2-Ethyl-hexanol	Residue
20	None	98.2	6.5	28.9(1.2)	20.7(0.4)	4.1(29.5)	3.0(22.4)	0 (0)	29.0(1.7)	0(2.3)	0(26.6)	14.3(15.9)
21	Pyridine (2.0)	(95)	5.1	22.0(1.2)	22.8(2.7)	3.0(16.0)	1.0(23.5)	5.0(0)	33.2(1.0)	0(3.8)	0(39.8)	13.0(12.0)
22	*N*,*N*-Dimethylaniline (2.0)	99.1	10.6	29.2(0.9)	20.2(0.5)	4.9(30.4)	1.4(21.7)	2.1(0)	28.8(3.1)	0(2.8)	0(26.6)	13.4(14.0)

a) The numerals in brackets correspond to the product after the hydrogenation in the usual way.
The reaction conditions were quite the same as in the runs in Table II. The initial charge included 0.2 ± 0.01 mol. C_3H_6, 0.068 mol. n-C_3H_7CHO, 0.4 mmol. $Co_2(CO)_8$, and 1.6 mmol. $Mg(OCH_3)_2$, without or with an organic base.

TABLE IV. HYDROGENATION OF MODIFIED OXO PRODUCT WITH 2 : 1 SYNTHESIS GAS IN THE PRESENCE OF IRON PENTACARBONYL

Exp. No.	Mg methylate mmol.	Pyridine mmol.	$Fe(CO)_5$ mmol.	k 10^{-2} min^{-1}	Product composition, wt.%								
					n-C_3H_7CHO	i-C_3H_7CHO	n-C_4H_9OH	i-C_4H_9OH	$C_7H_{13}CHO$	$C_7H_{15}CHO$	2-Ethyl-4-methylpentanol	2-Ethyl-hexanol	Residue
23	0.8	3.0	None	3.1	7.3	22.4	3.6	0.9	17.6	25.8	0	0	22.4
24	0.8	3.0	0.4	—	3.3	1.6	20.6	24.1	0	3.5	1.9	27.6	17.4
25	0.8	3.0	0.8	2.9	2.3	1.6	17.5	23.3	0	4.5	2.3	29.9	18.6
26	0.8	3.0	1.6	—	1.3	1.0	20.0	25.3	0	3.0	2.3	28.8	18.3
27	0.8	3.0	3.0	3.2	2.2	1.8	16.5	21.1	0	2.2	2.9	29.5	23.8
28	0.8	0	0.8	16.4	2.2	0.4	28.2	23.2	0	0	1.9	21.0	23.1
29	0.8	1.0	0.8	8.3	2.9	1.0	24.9	23.6	0	3.2	2.2	22.3	19.9
30	0.8	2.0	0.8	5.5	2.4	0.6	23.1	23.4	0	2.1	2.7	29.4	16.3
31	0.8	4.0	0.8	3.3	2.0	2.5	14.2	22.7	0	5.9	3.5	28.5	20.7
32	1.2	4.0	0.8	3.0	3.2	3.5	15.6	25.3	0	5.7	3.7	35.3	7.7
33	1.6	4.0	0.8	4.9	2.2	1.1	15.8	27.2	0	2.7	3.5	40.1	7.4

The initial charge contained 0.2 ± 0.01 mol. C_3H_6, 0.068 mol. n-C_3H_7CHO, and 0.4 mmol. $Co_2(CO)_8$, besides $Mg(OCH_3)_2$ and pyridine.

TABLE V. DICOBALT OCTACARBONYL REMAINING UNDECOMPOSED AFTER HYDROGENATION OF OXO PRODUCT

Exp. No.	Gas composition H_2 : CO	$Fe(CO)_5$ mmol.	Undecomposed metal carbonyl		Product composition, wt.%									
			Co mg. atom/l.	Fe eq.	n-C_3H_7CHO	i-C_3H_7CHO	n-C_4H_9OH	i-C_4H_9OH	n-$HCO_2C_4H_9$	i-$HCO_2C_4H_9$	$C_7H_{15}CHO$	n-$C_3H_7CH(OC_4H_9)_2$	i-$C_3H_7CH(OC_4H_9)_2$	Residue
34	1 : 1	None	1.2	0	5.0	2.5	57.6	9.5	3.1	2.0	2.8	7.7	2.7	7.1
35	1 : 1	1.6	5.9	11.0	0.6	0.1	72.6	11.7	3.8	2.4	2.2	2.3	0	4.3
36	1.5 : 1	None	1.0	0	10.1	6.4	42.8	7.6	1.9	1.2	2.2	16.7	7.0	4.1
37	1.5 : 1	1.6	3.8	10.6	0.7	0.1	73.7	12.7	4.1	2.1	1.6	1.0	0	4.0
38	2 : 1	None	0.5	0	8.4	4.3	53.5	7.8	2.7	1.3	3.8	9.3	3.2	5.7
39	2 : 1	1.6	1.8	10.3	0.6	0.1	72.0	12.9	3.3	1.7	2.4	1.4	0	5.6

The initial charge consisted of 0.44 ± 0.01 mol. C_3H_6, 0.5 mol. n-C_3H_7CHO, and 0.8 mmol. $Co_2(CO)_8$, without or with 1.6 mmol. $Fe(CO)_5$.

minor amounts of butanols. Wender et al.[15] pointed out that the hydrogenation of butyraldehyde to butanol proceeded smoothly at 185°C under 200 atm. of the synthesis gas, but they presented no experimental data on the rate. According to our preliminary experiments, the hydrogenation, even at this high temperature, proceeded at a rate lower than that as did propylene hydroformylation at 150°C, when a considerable amount of aldehydes, particularly of dimer aldehydes, used to remain after hydrogenation of an hour. A higher temperature, for instance, one of 200°C might naturally be expected to increase the hydrogenation rate. Nevertheless, the hydrogenation stopped soon after the temperature rose to 200°C, because of the decomposition of the dicobalt octacarbonyl to cobalt metal (cf. Exp. No. 23 in Table IV). In this connection, Berty et al.[7] had already stated that not only the simple elevation of temperature to 200°C, but also the higher pressure of 300 atm., could barely bring about the hydrogenation of octylaldehyde. The higher pressure, however, was not economical from a practical point of view.

Previous data available for the equilibrium concentration of metal carbonyls under carbon monoxide, of dicobalt octacarbonyl by Berty et al.,[7] and of iron pentacarbonyl by Pichler et al.[16] indicated that the latter metal carbonyl was more stable at a high temperature at a fixed carbon monoxide pressure. Moreover, our previous paper[17] reported that iron pentacarbonyl was a catalyst capable of hydrogenating methylacrylate to methylpropionate with a gas mixture including hydrogen and carbon monoxide. On the basis of these findings, an attempt has been made to carry out the hydroformylation in the presence of iron pentacarbonyl, besides that of dicobalt octacarbonyl and magnesium methylate, and then to effect, without any treatment of the oxo product, the hydrogenation of the resulting aldehydes to the corresponding alcohols by the simple elevation of the temperature to 200°C.

In the experimental runs, $2H_2 : 1CO$ synthesis gas at 200 kg./cm^2 was used in place of the 1 : 1 synthesis gas used in the preceding runs, since hydrogen and carbon monoxide were to be consumed in the ratio of 2 : 1. The hydroformylation was conducted at 150°C for an hour, followed by a rapid temperature rise to 200°C, which was accompanied by a temporary pressure rise to 210~217 kg./cm^2. Thereafter, the pressure was fixed at 200 kg./cm^2, which level was maintained during the hydrogenation period of an hour by the continuous introduction of the 2 : 1 synthesis gas from the pressure vessel.

The results are listed in Table IV. It has now been proved that in the presence of iron pentacarbonyl almost all C-8 as well as C-4 aldehydes are hydrogenated to the corresponding alcohols, whereas in its absence the aldehydes are left unhydrogenated. Pyridine again effects the dimerization favorably, resulting in a greater yield of C-8 alcohols, but it, in this series of runs, decreases the rate of hydroformylation to some extent (cf. Exp. Nos. 28, 29, 30, and 31). The yield of C-8 alcohols is increased by increasing the amount of magnesium methylate (cf. Exp. Nos. 31, 32, and 33).[18]

It has, however, remained unclarified whether cobalt carbonyl or iron carbonyl is the catalyst for the hydrogenation. It may be plausible that part of the cobalt carbonyl, at least, should be left as such in the product after the hydrogenation if the carbonyl does catalyze the hydrogenation. To confirm this, the carbonyl content in the product was determined. The hydroformylation and hydrogenation procedures were similar to those described just above, but they differed in some details; the runs were made with no modifiers for aldehyde dimerization, and in the hydrogenation stage hydrogen was supplied from another pressure vessel. Moreover, caution was exercised to avoid contamination of the product because of the corrosion of the autoclave material with carbon monoxide; this was avoided by using another shaking 400 cc. autoclave, the whole inner surface of which was lined with titanium. After the hydrogenation, the carbonyls of cobalt and, at the same time, of iron remaining dissolved in the liquid products were determined in the following way; the carbonyls in the filtrate free from finely divided metal precipitates were quantitatively decomposed into sulfates with sulfuric acid, and the resulting metal ions were determined by means of a chelate titration method using EDTA.

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[15] I. Wender, M. Orchin and H. H. Storch, *J. Am. Chem. Soc.*, **72**, 4842 (1950).

[16] H. Pichler and H. Wallenda, *Brennstoff-chem.*, **21**, 133 (1956).

[17] H. Uchida and K. Bando, This Bulletin, **29**, 953 (1956).

[18] Most of the residue in Table IV is probably a mixture of compounds whose individual boiling points are higher than that of octylalcohol. The porducts from runs Nos. 24-26 and 29-33 were collected and removed from octylalcohol, together with the lower boiling constituents, by distillation. The composition of the material at the bottom, amounting to 14% of the total product, was then determined by means of a gas chromatographic procedure (for details of the procedure, cf. our previous paper[19]); it proved to include 4.5 2-ethylhexyl-isobutyrate, 12.3 2-ethylhexyl-*n*-butyrate, and 19.0 2-ethyl-1, 3-hexanediol in wt. %.

[19] A. Matsuda and H. Uchida, *Rpt. Gn't. Chem. Ind. Research Inst. Tokyo*, **57**, 50 (1962).

The product obtained from a raw material consisting of 0.5 mol. *n*-butyraldehyde, 0.44± 0.01 mol. propylene, 0.8 mmol. dicobalt octacarbonyl, and 1.6 mmol. iron pentacarbonyl should contain respective carbonyls equivalent to about 20 mg. atom cobalt and 20 mg. atom iron per liter.

The results, as summarized in Table V, indicate that only minute amounts of dibutyracetals and of butyraldehydes remain unhydrogenated in the product from the raw material including iron pentacarbonyl, while a greater amount remains in the product from the raw material including no iron pentacarbonyl, and that under relatively high pressures of carbon monoxide, the oil-soluble cobalt in the former product is about three times the amount of that in the latter product. The hydrogen absorption, in the absence of iron pentacarbonyl, stopped in a short time after the temperature was raised to 200°C, but in the presence of iron pentacarbonyl, it took place continuously until the hydrogenation was nearly completed. An additional fact sheds light on the role played by iron pentacarbonyl; a hydrogenation run of *n*-butyraldehyde (3 mol.) carried out in the presence of iron pentacarbonyl (3 mmol.) alone at 200 kg./cm^2 of the 1 : 1 synthesis gas showed scarcely any absorption of hydrogen, even after a prolonged reaction of 10 hr.[20] These facts lead to the conclusion that iron pentacarbonyl is not the real catalyst for the hydrogenation of the aldehyde but that it contributes to the hydrogenation by suppressing, at high temperatures, the decomposition of the dicobalt octacarbonyl that does catalyze the hydrogenation.

Summary

Among the modifiers which have been tested, magnesium compounds are the most effective in producing a great amount of dimer aldehydes in the course of the propylene hydroformylation. The addition does not result in any reduction of the hydroformylation rate at 150°C. A certain amount of C-4 aldehydes had already been dimerized in the presence of dicobalt octacarbonyl alone, but the amount of dimerized aldehydes is greatly increased by the further addition of magnesium compounds, the total amount exceeding the sum of the amounts obtainable in the presence of either one of them. Moreover, the addition of an organic base further increases the yield of dimer aldehydes to some extent.

When starting with the raw material also containing iron pentacarbonyl, the hydrogenation of the aldehydes with the synthesis gas can be accomplished by the simple elevation of the temperature to 200°C. In the hydrogenation stage, iron pentacarbonyl does not behave as the catalyst for itself, but it contributes to the hydrogenation by suppressing, at that high temperature, the decomposition of the dicobalt octacarbonyl that is the real catalyst.

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[20] The product consisted of 12.1 *n*-butyraldehyde, 2.3 *n*-butanol, 1.1 C-8 saturated aldehydes, 3.4 *n*-butyr-*n*-butyrate, 67.5 C-8 unsaturated aldehydes, and 13.5 residue in wt. %.