The Preparation of Dimer Aldehydes and Dimer Alcohols in an Oxo Reactor. II. The Initial Rate of the Hydroformylation of Propylene in the Presence of Magnesium Methylate as a Modifier

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The preceding paper1) of this study reported that the addition of magnesium methylate to the starting material for propylene hydroformylation produced C-8 aldehydes in a good yield, without causing any reduction in the initial rate at 150°C. These results alone, however, were not enough to enable us to understand well the effect of magnesium methylate addition upon the initial rate. This paper will, therefore, present more accurate and comprehensive data on the initial rates in a certain range of temperatures which are prevalent in practical hydroformylation runs. The discussion of the results obtained will suggest other catalysts for hydroformylation in the presence of magnesium methylate besides that of cobalt carbonyl.

Experimental

The hydroformylation run was conducted, by use of the same 300 cc. autoclave, in essentially the same way as in the preceding paper,1) except that the addition of dicobalt octacarbonyl was modified in such a manner that a more accurate determination of the initial rate was possible: Before the autoclave was covered up, an amount of dicobalt octacarbonyl crystals was placed in a small saucer (0.5 cc.) of stainless steel held on a wing of a stirring mechanism. Having been charged with a *n*-butyraldehyde solution of magnesium methylate besides the carbonyl in the saucer, the autoclave was flushed with a synthesis gas of 1 : 1 H_2-CO, some propylene was introduced, and then the autoclave was pressured with the synthesis gas from a pressure storage, to which the autoclave was connected by way of a needle valve, to about 140 kg./cm^2 at room temperature. The autoclave was heated to the reaction temperature, and then a small amount of the synthesis gas was added from the pressure storage to raise the total pressure to 200 kg./cm^2. The instant the stirring mechanism was started, the saucer was allowed to fall down from the wing to dissolve the dicobalt octacarbonyl in the solution, whereupon the hydroformylation reaction set in. During the run, the synthesis gas was continuously supplied through the needle valve from the pressure storage into the autoclave in order to maintain the total pressure at 200 kg./cm^2. The accompanying pressure drops in the pressure storage with time were recorded. The recorded data might serve as a measure of the initial rate provided that the data could be interpreted in terms of a reasonable evaluation of the amount of synthesis gas consumed by the hydroformylation itself.

After the reaction period of an hour, the autoclave was cooled in running water. The gaseous material was purged, metered, and analyzed for the unchanged propylene in order to obtain the propylene conversion rate. The analysis of propylene as well as that of constituents in the liquid product was made in the way described in the preceding paper.1) The raw materials used in this study were obtained from the same sources as those in the preceding study.1)

In order to obtain a picture of the catalyst in the simultaneous presence of cobalt carbonyl and magnesium methylate, both the ratio of combined carbon monoxide (mole) to the total cobalt (atom) (hereafter denoted by CO_c/Co) and the ratio of cobalt (atom) existing as a carbonyl anion to the total cobalt (atom) (hereafter denoted by Co_{an}/Co) were determined, together with an infrared spectrum, on the liquid samples at the earlier stages of runs with and without magnesium methylate. The runs for this purpose were made by means of another autoclave (100 cc. in volume) of the same construction but lined with titanium over the whole inner surface lest the liquid samples should be contaminated with metal carbonyls from the autoclave material. From the beginning a few samples of a small portion (ca. 5 cc.) of the liquid product were sucked at five-minute intervals into a titanium dip-tube withdrawn out of the autoclave by passing them through a stainless steel tube cooled in ice, and subjected to immediate determination. The

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1) H. Uchida and A. Matsuda, This Bulletin, 36, 1351 (1963).

combined carbon monoxide was determined according to the method of Sternberg et al.[2] who measured the volume of the carbon monoxide liberated by the addition of excess iodine, and the carbonyl anion according to the method of Iwanaga,[3] who titrated the sample with an acetic acid-toluene solution of methyleneblue. The infrared spectrum was determined by means of a rock salt prism using *n*-butyraldehyde as the reference solution.

Results and Discussion

The Rate of Hydroformylation. — In the preceding paper,[1] the initial rate constant, k, for the batchwise run of propylene hydroformylation was represented by the following formula:

$$k=(1/t)\ln(c_0/c_t)=(1/t)\ln[c_0/(c_0-V/2)] \qquad (1)$$

where t (min.) was the reaction time, c_0 (mol.) was the initial amount of propylene, c_t (mol.) was the amount of propylene at reaction time t, and V (mol.) was the amount of synthesis gas introduced from the pressure storage into the autoclave at reaction time t. The formula, however, was rather a conventional one because V, as measured by the drop in pressure of the pressure storage, was simply put as equal to $2(c_0-c_t)$ (mol.). In fact, however, V consisted of two portions of the synthesis gas, one (V_r, mol.) that consumed by the hydroformylation reaction itself and the other (V_0, mol.) that necessary to compensate for the fall in propylene partial pressure as the reaction proceeded. V_r, in place of V, should have been identical with $2(c_0-c_t)$. In this connection, Eq. 1 will be improved to give a more accurate expression of k.

Under the assumption that the propylene partial pressure, p, is proportional to the total propylene content,[4] the drop in propylene partial pressure (p_0-p) is written as:

$$p_0-p=p_0(c_0-c_t)/c_0 \qquad (2)$$

where p_0 is the initial propylene partial pressure under the reaction conditions. Taking Eq. 2 into consideration, V_0 is given by Eq. 3:

$$V_0=a(p_0-p)=ap_0(c_0-c_t)/c_0 \qquad (3)$$

In the above equation, a is a coefficient whose value is dependent on the reaction temperature. Since $V=V_r+V_0$, V is then expressed as follows:

$$V=2(c_0-c_t)+ap_0(c_0-ct)/c_0 \qquad (4)$$

The substitution of the c_t obtainable from Eq. 4 into Eq. 1 results in the following expression of k:

$$k=(1/t)\ln\{c_0/[c_0-V(2+ap_0/c_0)]\} \qquad (5)$$

To calculate Eq. 5 for k, ap_0 (mol.) at the present reaction conditions should be determined first. The determination, including some experimental measurements, has resulted in the respective values of 0.140, 0.155, 0.178, and 0.191 mol. at 130, 140, 150, and 160°C, provided that the initial charges of propylene and *n*-butyraldehyde in the autoclave are 0.22 and 0.068 mole respectively and the total pressure is 200 kg./cm^2.

Meanwhile, let us explain the procedure for calculating ap_0. The Benedict-Webb-Rubin equation of state[5] can give p_0 if the initial propylene density, d_0, in the autoclave at the reaction conditions is known. To obtain d_0, the initial propylene mole fraction, s_0, in the gas phase at the reaction conditions has only to be determined experimentally, since d_0 (g. mol./l.) is expressed by the formula:

$$d_0=n_0/V=s_0\boldsymbol{P}/z\boldsymbol{RT} \qquad (6)$$

where n_0 is the initial propylene content (g. mol.) in the gas phase under the reaction conditions, V (l.) is the volume of the gas phase in the autoclave, P (atm.) is the total pressure, and z is the compressibility factor of the gaseous mixture under the reaction conditions. The determination of s_0 was made on four samples withdrawn from the gas phase at the temperatures of 130, 140, 150, and 160°C in the autoclave; the initial charges of the samples were 0.22 mol. propylene and 0.068 mol. *n*-butyraldehyde, with neither cobalt carbonyl nor magnesium methylate, and they were subsequently added with the synthesis gas to 200 kg./cm^2. Once s_0 is obtained, z is evaluated as ca. 1.02 at 200 kg./cm^2 over the 130 to 160°C temperature range; consequently, d_0 is determined by the aid of Eq. 6. The substitution of the values of d_0 into the Benedict-Webb-Rubin equation results in the corresponding values of p_0, which are 18.7, 21.2, 25.0 and 27.5 atm. at 130, 140, 150 and 160°C respectively. The determination of ap_0 is then possible by a simple calculation.

Findings on the initial rates of hydroformylation over a temperature range from 130 to 160°C are exemplified in Figs. 1 and 2 as plots of $\ln[c_0/\{c_0-V/(2+ap_0/c_0)\}]$ vs. t. Throughout the runs, the initial charges of *n*-butyraldehyde,

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2) H. W. Sternberg, I. Wender and M. Orchin, *Anal. Chem.*, **24**, 174 (1952).

3) R. Iwanaga, This Bulletin, **35**, 247 (1962).

4) At the earlier stages of the present experiment, a major part of the propylene exists in the gaseous phase.

5) $p_0=RTd_0+(B_0RT-A_0-C_0/T^2)d_0^2+(bRT-a)d_0^3+a\alpha d_0^6+[cd_0^3(1+\gamma d_0^2)\exp(-\gamma d_0^2)]/T^2$ (cf. 6)).
where R is the gas constant, T is the temperature (°K), and B_0, A_0, C_0, b, a, c, α, and γ are constants whose values with respect to propylene are available from the literature.[7]

6) E. D. Comings, "High Pressure Technology," McGraw-Hill Book Co. N. Y. (1956), p. 251.

7) Ibid., p. 485.

propylene, and dicobalt octacarbonyl were kept constant at the respective amounts of 0.068, 0.22 mol., and 0.4 mmol., but magnesium methylate was varied in amount at 0.8 mmol. intervals between 0 and 3.2 mmol. In each run the plot is linear, and the initial rate constant, *k*, is readily evaluated from the slope of the plot. For each series of runs with a fixed amount of magnesium methylate, an Arrhenius plot is drawn, as shown in Fig. 3. In the figure the plots intersect with one another at A, where $1/T$ is 423°K. This plainly indicates that the initial rate constant, and thus the initial rate at 150°C, remains unchanged, independent of the amounts of magnesium methylate added, but that within the amount of about 2.4 mmol. the initial rates at the reaction temperatures below 150°C

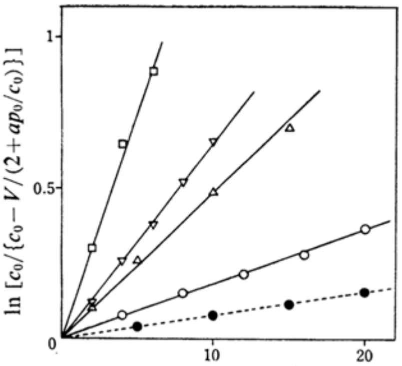


Fig. 1. Initial rate of propylene hydroformylation without magnesium methylate.
—○— Reaction temperature, 130°C, $k=1.8\times10^{-2}$ min^{-1}
—△— 140°C, 4.8×10^{-2} min^{-1}
—▽— 150°C, 6.5×10^{-2} min^{-1}
—□— 160°C, 15.0×10^{-2} min^{-1}
···●··· 140°C, 0.8×10^{-2} min^{-1}
The dotted line indicates the initial rate in the presence of an amount of 2-ethylhexenal.

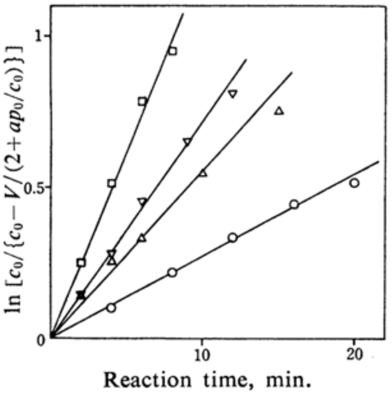


Fig. 2. Initial rate of propylene hydroformylation with magnesium methylate (0.8 mmol.).
—○— Reaction temperature, 130°C, $k=2.7\times10^{-2}$ min^{-1}
—△— 140°C, 5.6×10^{-2} min^{-1}
—▽— 150°C, 7.2×10^{-2} min^{-1}
—□— 160°C, 12.4×10^{-2} min^{-1}

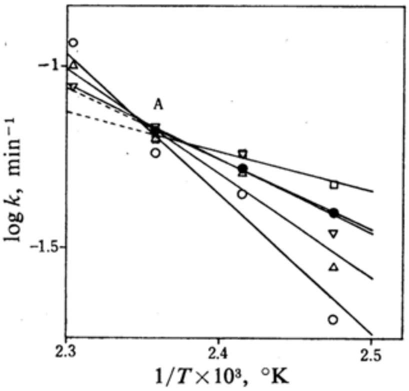


Fig. 3. Arrhenius plot of initial rate constant.
—○—: Magnesium methylate (mmol.), 0
—△—: 0.8 —△—: 1.6
—□—: 2.4 —●—: 3.2

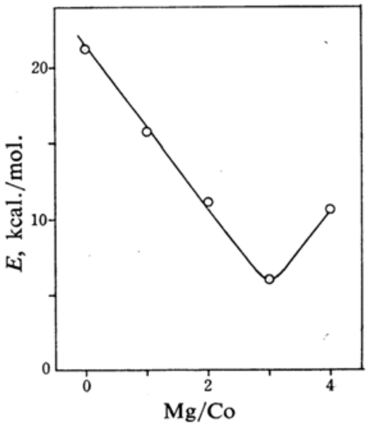


Fig. 4. Activation energy of propylene hydroformylation as function of Mg/Co (atom).

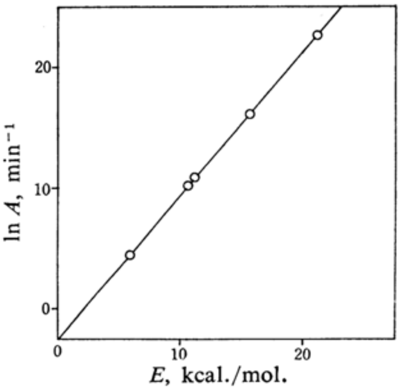


Fig. 5. Plot of logarithm of frequency factor against activation energy.

increase more markedly as the amount of magnesium methylate is increased, whereas the situation is reversed above 150°C.

On the basis of the plots in Fig. 3, the activation energies, E, as well as the frequency factors, A, of hydroformylation reactions with varying amounts of magnesium methylate can be calculated. A plot of E vs. Mg/Co (atom ratio) in the raw material, as illustrated in Fig. 4, indicates that E diminishes with Mg/Co at first, passes through a minimum at Mg/Co=3 and then rises. Moreover, a plot of $\ln A$ against E appears to be linear, as is shown in Fig. 5. The linear relationship is represented by the following equation:

$$\ln A = E/\boldsymbol{R}\Theta + \ln A' \qquad (7)$$

where Θ is a constant of the proportionality with the dimension of temperature and A' is another constant, their respective values being calculated as 423°K (150°C) and 0.074 min^{-1}. This relationship indicates that a compensation effect appears in a particular manner that obeys the "Theta Rule."[8)]

The compensation effect has been reported in a number of liquid-phase reactions, such as hydrolysis and esterification in the presence of inorganic acid, where a series of differently substituted compounds or of different kinds of solvents was used (cf. 9) and 10)). Nevertheless, no paper, so far as we are aware, has ever dealt with the compensation effect taking place in a series of liquid-phase reactions with different catalyst compositions. On the other hand, there are many examples of gas-solid heterogeneous catalysis where the compensation effect appears as the catalyst compositions are changed. According to Cremer[11)] the effect on the heterogeneous catalysis can be ascribed to the simultaneous presence of two or more kinds of active sites participating in the reaction, with different activation energies and frequency factors. Extending the view of Cremer to the present liquid-phase reaction, the compensation effect can be interpreted as coming from the presence of two kinds of catalysts, presumably one being the carbonyl of cobalt and the other being the compound into which the carbonyl and magnesium methylate have been combined. At first sight, one may be apt to consider the latter catalyst as consisting of three moles of magnesium methylate and one mole of the carbonyl (cf. Fig. 4), but a detailed examination of the chemistry of the catalyst itself reveals that this is not necessarily the case, as will be mentioned in the next section.

Catalysts in the Presence of Magnesium Methylate.—The CO_c/Co and Co_{an}/Co ratios were determined for the samples at earlier stages of the runs using 0.136 mol. of *n*-butyraldehyde, 0.1 mol. of propylene, and 0.6 mmol. of dicobalt octacarbonyl, either without or with 3.6 mmol. of magnesium methylate (Mg/Co=3). The runs were conducted at 150°C at 200 kg./cm^2. The results are cited in Table I. In accordance with the results of Heck and Breslow,[12)] the value of CO_c/Co is always about three, independent of whether magnesium methylate was added or not. In constrast to this, Co_{an}/Co is zero or an extremely low value in the absence of magnesium methylate, while in its presence it attains to such higher values as 0.2 to 0.34. The carbonyl anion, as is well known,[13)] would not be detected in the reaction medium at the earlier stage of the usual hydroformylation where a considerable amount of olefin remains. Accordingly, the carbonyl anion thus detectable in the present runs can be ascribed to that of a mixed metal carbonyl of $[Co(CO)_4]_2 \cdot Mg$ produced in a way similar to that in which the carbonyl of $[Co(CO)_4]_2Zn$[14)] is produced. The mixed metal carbonyl $[Co \cdot (CO)_4]_2Mg$, as well as $[Co(CO_4]_2Zn$, can act as the catalyst for aldehyde dimerization, but it can not be the catalyst for hydroformylation. Moreover, it should be emphasized that only one-third to one-fifth of the cobalt, not all of the cobalt, participates in producing the mixed metal carbonyl, even though magnesium methylate is added in the great excess of Mg/Co=3. This may be the reason why magnesium methylate produced dimer aldehydes in a good yield, without exercising an

TABLE I. RATIOS OF COMBINED CARBON MONOXIDE AND COBALT AS CARBONYL ANION TO TOTAL COBALT

Reaction time min.	With $Mg(OCH_3)_2$[a)]		Without $Mg(OCH_3)_2$	
	CO_c/Co	Co_{an}/Co	CO_c/Co	Co_{an}/Co
ca. 1	2.7	0.19	2.9	0
5	3.0	0.34	—	—
10	2.9	0.22	2.9	0.05

a) Magnesium methylate was added in the amount corresponding to Mg/Co (atom ratio) of 3.

[8)] M. Boudart, *Chem. Eng. Prog.*, **57**, No. 8, 33 (1961).

[9)] J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

[10)] R. F. Brown, ibid., **27**, 3015 (1962).

[11)] E. Cremer, "Advances in Catalysis," VIII, Academic Press, N. Y. (1955), p. 85.

[12)] R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

[13)] M. Orchin, L. Kirch and I. Goldfarb, ibid., **78**, 5450 (1956).

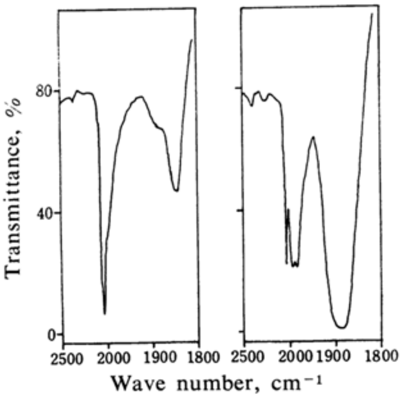
[14)] H. Hieber and H. Schulten, *Z. anorg. u. allgem. Chem.* **243**, 145 (1929).

TABLE II. PROPYLENE CONVERSION AND COMPOSITION OF HYDROFORMYLATION PRODUCT

Expt. No.	Reaction temp., °C	$Mg(OCH_3)_2$ mmol.	Propylene conversion %	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	130	none	94.6	56.7	20.1	2.0	0.3	0	2.1	18.8
2	140	none	99.4	51.2	21.9	2.2	1.2	0	3.9	19.6
3	150	none	99.5	53.4	21.0	2.6	1.0	0	4.7	17.3
4	160	none	—	41.6	21.0	5.5	2.5	0	7.3	22.1
5	130	0.8	93.4	45.3	20.7	2.5	0.9	4.8	9.3	16.5
6	140	0.8	98.6	41.4	22.7	2.8	1.3	4.0	14.8	13.0
7	150	0.8	99.7	34.7	22.7	4.0	3.0	0	21.0	14.6
8	160	0.8	—	29.7	21.1	5.9	3.2	0	21.8	18.3
9	130	1.6	91.4	38.5	20.0	2.3	1.0	8.5	17.5	12.2
10	140	1.6	97.7	33.8	22.6	3.0	2.1	5.0	20.8	12.7
11	150	1.6	99.2	30.7	22.6	4.2	3.0	1.1	24.3	14.1
12	160	1.6	—	26.9	22.4	6.4	4.6	0	22.9	16.8
13	130	2.4	90.9	33.0	21.1	2.3	0.8	11.1	18.0	13.7
14	140	2.4	96.9	29.8	22.3	3.4	1.2	5.8	24.3	13.2
15	150	2.4	98.9	25.4	23.2	4.4	1.6	1.5	31.6	12.3
16	130	3.2	87.3	28.6	19.3	2.3	1.0	12.7	18.0	18.1
17	140	3.2	94.5	23.6	23.2	4.2	1.2	7.2	28.0	12.6
18	150	3.2	98.4	23.1	22.6	4.3	1.6	2.0	33.2	13.2

unfavorable effect on the initial rate of hydroformylation.

So far as the afore-mentioned results are concerned, it remains undetermined whether the remaining portions of cobalt carbonyl and of magnesium methylate exist separately or as a complex compound into which they have combined. In this connection, a possible interpretation of the compensation effect has suggested a kind of catalyst for hydroformylation besides cobalt carbonyl. The suggestion is supported by the following results on the infrared spectrum measurement: The infrared spectrum of the reaction product (e. g., the product at 10 min. interval from beginning) without magnesium methylate is similar to, though not identical with, that of dicobalt octacarbonyl (cf. 15)), but the spectrum of the reaction product with magnesium methylate differs markedly from that described just (compare Fig. 6 with Fig. 7[16]). The latter spectrum contains characteristic peaks at 1991 and 1974 cm^{-1} and a band at 1891 cm^{-1} which is assignable to the carbonyl anion of the mixed metal carbonyl,[17] besides a band at 2030 cm^{-1} which also appears in the former spectrum but is much reduced in intensity. The marked difference thus observed between the two spectra indicates a bonding taking place between cobalt carbonyl and magnesium methylate. However, nothing more decisive can be said about the composition of the compound, or of the catalyst, because the data on the equilibrium, such as $1/2\cdot Co_2(CO)_6 + xMg(OCH_3)_2 \rightleftharpoons [Co(CO)_3]^{-\delta}[Mg(OCH_3)_2]_x^{+\delta}$, are not yet available.



A B

Figs. 6 and 7. Infrared spectra of reaction products starting with raw materials (A) without and (B) with magnesium methylate respectively.

Propylene Conversion and Product Composition.—Table II summarizes the propylene conversion and the product composition after an hour's reaction period. The rate of conversion tends to lower with Mg/Co, and this tendency appears more clearly at the lower reaction temperatures, where the content of unsaturated C-8 aldehyde is larger. It is to be expected that the conversion should be low

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15) R. A. Friedel, I. Wender, S. L. Shuffer and H. W. Sternberg, *J. Am. Chem. Soc.*, **77**, 3951 (1955).

16) Magnesium methylate alone does not give any absorption band in the region under investigation. The band at 1841 cm^{-1} in the spectrum of Fig. 6 may be assingnable to a bridge carbonyl of $Co_2(CO)_6$ (cf. 15)).

17) O. Vohler, *Chem. Ber.*, **91**, 1161 (1958).

TABLE III. COMPOSITION OF PRODUCT AFTER HYDROGENATION

Expt. No.	Product composition, wt.%							
	n-C_3H_7CHO	*i*-C_3H_7CHO	*n*-C_4H_9OH	*i*-C_4H_9OH	$C_3H_7COOC_4H_9$	C-8[a] alcohol(1)	C-8[a] alcohol(2)	Residue
1	1.5	0.8	53.8	16.2	1.8	0	8.7	17.2
3	0.4	0.1	52.4	19.4	1.1	0	7.8	18.1
5	0.6	0.5	40.4	15.8	2.5	0.6	25.5	14.1
7	0.5	0.2	31.5	17.3	2.1	2.5	27.8	18.1
9	0.7	0.3	37.0	15.3	1.8	1.4	29.4	14.1
11	0.4	0.2	27.3	18.5	3.2	2.4	29.5	18.5
13	0.6	0.3	32.6	15.9	1.9	1.5	32.7	14.5
15	0.5	0.3	25.9	18.4	1.2	3.0	32.1	18.6
16	0.7	0.2	30.0	15.9	1.8	1.7	35.6	14.1
18	0.6	0.3	24.1	18.6	1.3	2.6	33.7	18.8

a) C-8 alcohol(1) and C-8 alcohol(2) stand for 2-ethyl-4-methylpentanol and 2-ethylhexanol respectively.

in the presence of the unsaturated aldehyde because cobalt carbonyl and the unsaturated aldehyde combine into a catalytically inactive compound. This was confirmed with an experimental run starting with a raw material containing a some considerable amount of 2-ethyl-hexenal (0.05 mol.). The results, as shown by the dotted line in Fig. 1, reveal that the unsaturated aldehyde not only lowers the propylene conversion but also retards the initial rate of hydroformylation. However, it should be noticed that the retarding effect on the initial rate need not be considered with respect to the present data, since the amount of unsaturated aldehyde at the earlier stage might be too small to have any effect on the initial rate. In fact, the effect in the low temperature range is of a kind opposite to what one might expect.

Within the Mg/Co range of the present study, the dimer aldehydes content increases with the ratio. The residue in the table stands for the sum of the matter not identified as yet; it may mainly consist of compounds whose distillation temperatures are above those of C-8 aldehydes. Table III gives the compositions of some final products after the hydrogenation of the products in Table II in the usual manner, using a Raney cobalt catalyst.

Summary

The effect of magnesium methylate addition upon the initial rate of propylene hydroformylation has been explained in terms of Arrhenius plots of the initial rate constants, and in terms of the activation energy as a function of Mg/Co. Moreover, the plot of the logarithm of the frequency factor vs. the activation energy appears to be linear, which indicates that a compensation takes place with respect to the initial rate in the presence of magnesium methylate. The extension of Cremer's view about the compensation effect in heterogeneous catalysis into this kind of liquid-phase reaction leads one to expect another catalyst besides that of cobalt carbonyl.

The determination of the cobalt carbonyl anion in the reaction product obtained from raw material either with no or with a large excess of magnesium methylate (Mg/Co=3) indicates that in the former product scarcely no cobalt is detectable as the carbonyl anion, whereas in the latter product a part of the cobalt exists as such. The anion is to be ascribed to that of a mixed metal carbonyl of $[Co(CO)_4]_2Mg$, which facilitates the production of dimer aldehydes. Further, the infrared spectrum of the latter product differs markedly from that of the former product. This may afford evidence for the other catalyst expected.

In addition, this paper has presented data on the propylene conversion and the compositions of reaction products before and after hydrogenation, data obtained with raw materials containing varying amounts of magnesium methylate.

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