Hydroformylation and Hydrogenation of Methylacrylate in Presence of Dicobalt Octacarbonyl or Iron Pentacarbonyl. Dependence of Reaction Rate on Partial Pressures of Carbon Monoxide and Hydrogen

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Introduction

In the presence of dicobalt octacarbonyl, ethylacrylate can readily be hydroformylated to β-carbethoxypropionaldehyde. The reaction was once investigated by H. Adkins et al.[1] and thereafter in greater detail by K. Ohashi et al.[2] More recently G. Natta[3] made a study on the hydroformylation of cyclohexene and obtained the remarkable result that the ratio of carbon monoxide to hydrogen in a gas mixture has a considerable influence upon the reaction rate. In this study the hydroformylation of methylacrylate has therefore been conducted by paying special attention to the effect of the gas composition on the rate.

In contrast to dicobalt octacarbonyl, iron pentacarbonyl was generally thought to be ineffective for the hydroformylation. Recently the effect of iron pentacarbonyl upon the isomerization of olefin due to the migration of a double bond-effect which is similar to that of dicobalt octacarbonyl, was however

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[1] H. Adkins and G. Kresek, *J. Am. Chem. Soc.*, **71**, 3051 (1949).

[2] K. Ohashi and S. Suzuki, *J. Chem. Soc. Japan (Ind. Chem. Sec.)*, **56**, 792 (1952), (in Japanese).

[3] G. Natta, *Brennstoff-Chem.*, **36**, 176 (1955).

found by A. Asinger et al.4), so far as the carbon monoxide pressure was comparatively low. The present paper also deals with the reaction that has been made between methylacrylate and gaseous mixtures comprising carbon monoxide and hydrogen in the presence of iron pentacarbonyl, with the expectation that some effect of the carbonyl on the reaction may appear.

Experimental Procedure

In the presence of dicobalt octacarbonyl or iron pentacarbonyl, the reaction between a gaseous mixture of carbon monoxide and hydrogen and a quantity of methylacrylate was conducted in an autoclave (1 l. in volume) of shaking type, at a constant pressure at a fixed temperature. The carbonyls were used for the reaction after they were dissolved in benzene. The rate of the reaction was estimated by the pressure decrease in a high pressure gas storage (1.6 l. capacity) from which the gas was continuously introduced into the autoclave in order that during the reaction the initial pressure in the autoclave might be maintained at the reaction temperature.

Since the use ratio of carbon monoxide to hydrogen in the reaction of hydroformylation was 1:1, the continuous supply of gaseous mixture comprising equal volumes of carbon monoxide and hydrogen into the autoclave causes scarcely any change of gas composition compared with the orginal gas composition in the autoclave. In this way a constant ratio of carbon monoxide to hydrogen of the gaseous mixture in the autoclave was kept throughout the reaction.

As for the reaction with dicobalt octacarbonyl, a reaction temperature of 110°C was preferred, at which the reaction proceeded with a measurable rate. At temperatures (100–104°C), a little lower than 110°C, the slow absorption of gas had already begun to take place. During this period of slow absorption, the gas was supplied from the gas storage into the autoclave up to the pressure which would be expected by steadily increasing temperature up to 110°C if there no absorption. The temperature rise from 100 to 110°C usually required about eight minutes. Once the temperature arrived at 110°C, both the temperature and the pressure were kept constant during further progress of the reaction.

β-carbmethoxypropionaldehyde could not be obtained in a yield as expected theoretically from the amount of gases absorbed in the reaction, and the maximum yield atained to only 80% of the theoretical*.

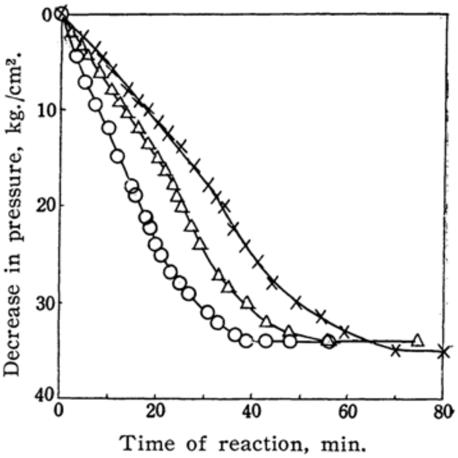
Dicobalt octacarbonyl was prepared according to the procedure by I. Wender et al.5): namely a slurry of 30 g. cobalt (II) carbonate in 200 cc. of petroleum-ether was treated with water-gas under a pressure of 200 kg./cm^2 in 1 l autoclave at 150°C for two hours, and the petroleum-ether solution of the carbonyl was cooled in dry ice for a short period of time, whereupon the crystalline dicobalt octacarbonyl separated. The crystallite was stored under the high pressure of carbon monoxide in a steel vessel, and a quantity of it was dissolved in 100 cc. of benzene immediately before use. Methylacrylate was supplied by the Toa Gosei Company and was 98% in purity. It was used without any further purification.

The reaction with iron pentacarbonyl was first conducted under conditions identical with those for dicobalt octacarbonyl, but it appeared soon that another kind of reaction took place, as will be described later. Iron pentacarbonyl was manufactured as was reported by one of the authors of this paper et al.6) previously.

Results

Hydroformylation of Methylacrylate in Presence of Dicobalt Octacarbonyl.—The reaction was first carried out at a fixed partial pressure of hydrogen with different partial pressures of carbon monoxide, and then at a fixed partial pressure of the latter with different partial pressures of the former.

In Fig. 1 are shown the results obtained in a series of the experiments carried out at a constant pressure of hydrogen with different partial pressures of carbon monoxide, using 92 g. of methylacrylate and 1.72 g. of dicobalt octacarbonyl in 100 cc. of benzene. Three curves in the figure reveal the pressure decrease in the gas storage



Every experiment was conducted at 110°C under a constant hydrogen pressure (97 kg./cm^2.), with different carbon monoxide pressures of 21 (—○—), 52 (—△—), and 99 kg./cm^2. (—×—) respectively.

Fig. 1. Decrease in pressure of gas storage with time.

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4) A. Asinger and O. Berg, *Ber.*, 88, 445 (1955).

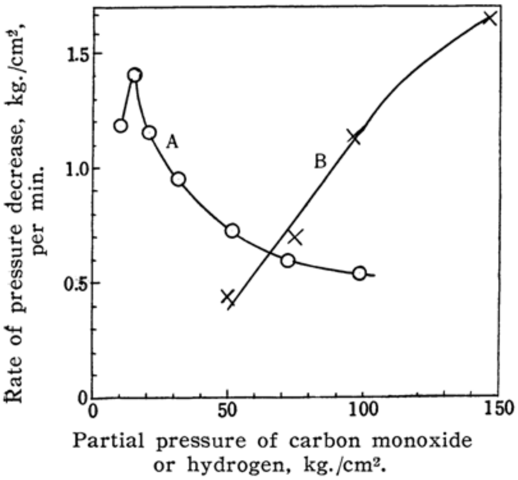
* The aldehyde was determined according to the procedure by H. Adkins et al.1) Even though the distillation was made, after an addition of a small quantity of hydroquinone, at as low a pressure and as rapidly as was possible, it seemed difficult to isolate aldehyde without a considerable loss.

5) I. Wender, H. Greenfield and M. Orchin, *J. Am. Chem. Soc.*, 73, 2659 (1951).

6) H. Uchida and T. Minegishi, *Rpt. Gvnt. Chem. Ind. Res. Inst. Tokyo*, 45, 1 (1950).

with time. A linear relation of the pressure decreae to time is observed during a time interval between the ten-minute and thirty-minute periods from the beginning of the reaction, and the slopes of the straight line give the rate of the reaction.

The dependence of the rate upon the partial pressure of carbon monoxide is given by curve A in Fig. 2. The rate attains the maximum value at a carbon monoxide pressure of 15 kg./cm³. At a lower carbon monoxide pressure of 11 kg./cm² the absorption of the gas remained incomplete, proceeding to only half the theoretically available extent and part of the carbonyl was found to decompose into precipitates of a composition which is unclarified as yet. At the carbon monoxide pressure higher than 15 kg./cm² the hydroformylation** proceeded to completion because of the absorption of the theoretical amount of the gas, but the absorption took place rather slowly. In this case any decomposition of the carbonyl was hardly recognized after the reaction.



A : hydrogen partial pressure, 97 kg./cm².

B : carbon monoxide partial pressure, 21 kg./cm².

Fig. 2. Relation of rate of hydroformylation to partial pressure of carbon monoxide (A) or hydrogen (B).

Curve B in Fig. 2 reveals the rate as a function of the hydrogen partial pressure at a fixed partial pressure of carbon monoxide. At hydrogen pressures higher than 75 kg./cm², the gas was absorbed in an amount just necessary for the hydroformylation of methylacrylate; however, at the lower pressures it was absorbed in only half the theoretical amount. In the former case the carbonyl persisted unchanged during the reaction, whereas in the latter case part of the carbonyl underwent decomposition. The high pressure of hydrogen has thus proved to be a requisite for the carbonyl to remain undecomposed in the reaction.

The tendencies presented here agree with the results obtained by G. Natta on the hydroformylation of cyclohexene.

A. R. Martin⁷⁾ proposed a rate equation for the case of hydroformylation of di-isobutene,

$$\text{initial rate} = ap_{H_2}/(bp_{H_2}+cp_{CO})\cdot[CO_2(CO)_8][C_8H_{16}]$$

where a, b, and c are constants. According to the equation the initial rate tends to decrease always with the rising carbon monoxide pressure. The tendency is in agreement with the present results obtained in a range of high carbon monoxide pressures, but is not so with those in a range of low pressures. In the latter case the carbonyl has been found to decompose during the reaction, and this is probably the reason why the rate begins to diminish again in this range. As for the dependence of the rate upon hydrogen pressure the equation suggests that, when b is not much greater than c, the rate tends to increase rather proportionally with the hydrogen pressure and then more slowly with the further increasing pressure. This is also consistent with the present results.

Hydrogenation of Methylacrylate in Presence of Iron Pentacarbonyl.—In the presence of iron pentacarbonyl, no reaction between methylacrylate and a gaseous mixture composed of carbon monoxide and hydrogen proceeded at 110°C, but at the higher temperature of 160°C the absorption of gas was found to take place if carbon monoxide partial pressure remained considerably low. Of the two gaseous reactants only hydrogen was absorbed to such an extent that, at the maximum absorption, the absorbed hydrogen amounted to one mole for one mole of methylacrylate, whereas the carbon monoxide was absorbed in extremely small amounts (0.03–0.04 mol.).

No absorption of hydrogen was observed in the reactions, either in the presence or absence of carbon monoxide conducted with iron catalysts such as the reduced one from iron oxide and the other one produced by thermal decomposition of iron pentacarbonyl.

The product of the reaction was confirmed as methylpropionate***.

In order to see the effect of the partial pressure of an individual gaseous component on the reaction rate, the reaction was conducted at a fixed hydrogen pressure with varying carbon monoxide pressures and with varying hydrogen

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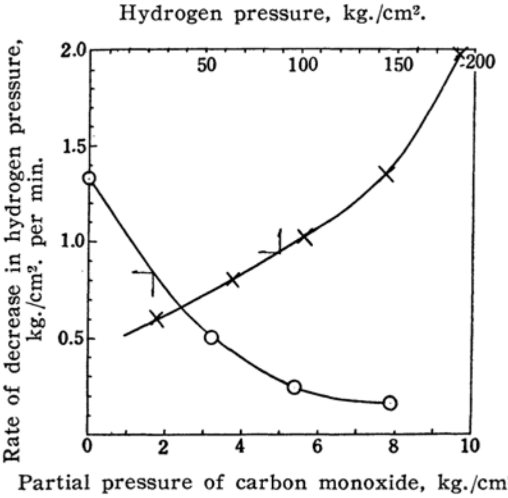
** Hydrogenation of β-carbmethoxypropionaldehyde as well as of methylacrylate seemed not to take place, as hydrogen was absorbed in an amount equal in mole to that of carbon monoxide.

7) A. R. Martin, *Chem. and Ind.*, **1536** (1954).

*** The confirmation was made as follows. Since the boiling temperatures of methylpropionate and benzene differed too little to permit the separation from each other by distillation, the synthesis of the product for the confirmation was carried out without any addition of benzene. In this case the hydrogen absorption proceeded to only three quaters of the theoretical extent. About 70% of the product distilled out at 78—80°C, leaving a higher boiling residue of polymerized products of methylacrylate. After the distillate had been freed from iron pentacarbonyl by adding mercuric chloride together with aceton and water, 70% of the distillate distilled out again at 79—79.5°C which corresponded to the b.p. of methylpropionate. The second distillate has a saponification value of 630. It contains a minute quantity (1%) of methylacrylate as determined according to the procedure by D.W. Beesing et al. using dodecanethiol (*Anal. Chem.*, **21**, 1073 (1949)).

pressures without an addition of carbon monoxide. During the reaction only hydrogen, but not a mixture of carban monoxide and hydrogen, was introduced into the autoclave from the gas storage. After the reaction without carbon monoxide the gaseous product contained about one per cent of carbon monoxide.

The initial rate obtainable from the initial tangent drawn to the curves for the pressure in the gas storage during the reaction vs. time is given in Fig. 3 as functions of carbon monoxide and hydrogen pressures respectively****. The reduction of methylacrylate by hydrogen takes place even in the presence of carbon monoxide at a pressure of 8 kg./cm². The lower the carbon monoxide pressure is, the higher the rate is; and the higher the hydrogen pressure is, the more rapidly the reaction proceeds.



Raw meterials: 92 methylacrylate and 10 g. iron pentacarbonyl in 100 cc. of benzene.

—○—: under a hydrogen partial pressure of 155 kg./cm².

—×—: in the absence of carbon monoxide.

Fig. 3. Relation of rate of hydrogenation to partial pressure of carbon monoxide or hydrogen pressure.

M. Orchin[8] stated that although ethylacrylate could be hydroformylated in the presence of dicobalt octacarbonyl it could not be reduced. The present results show that methylacrylate can be reduced in the presence of iron pentacarbonyl.

Summary

Hydroformylation of methylacrylate in the presence of dicobalt octacarbonyl was investigated by paying a special attention to the effect of varying ratios of carbon monoxide to hydrogen on the rate. The rate attains the maximum value at a certain partial pressure of carbon monoxide, and increases with the increasing partial pressure of hydrogen. The tendencies agree with the results obtained by G. Natta on the hydroformylation of cyclohexene. The rate equation proposed by A. R. Martin with respect to the rate of hydroformylation of di-isobutene can represent the tendencies observed in the present results.

In the presence of iron pentacarbonyl, methylacrylate has been found to be reduced to methylpropionate under high pressure of hydrogen containing carbon monoxide. The reduction becomes more difficult with the increasing partial pressure of carbon monoxide, but was made catalytically neither by an iron catalyst reduced from iron oxide nor by the one produced by the thermal decomposition of iron pentacarbonyl.

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**** In this series of experiments the absorption of gas at the temperature lower than 160°C was small and hence the initial tangent served for the representation of the initial rate.

[8] M. Orchin, *Advances in Catalysis*, 5, 391 (1953).