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THE INFLUENCE OF HYDROGEN AND
 CARBON MONOXIDE PARTIAL PRESSURES
 ON THE RATE OF THE HYDROFORMYLATION
 REACTION

Sir:

Previous work¹ in this laboratory on the kinetics of the hydroformylation reaction showed that the rate was proportional to the concentration of olefin and approximately proportional to the concentration of dicobalt octacarbonyl catalyst, while it was essentially independent of the pressure of synthesis gas ($H_2:CO = 1:1$) in the range of 120 to 380 atm. Since the reaction is thermodynamically possible at low pressures of synthesis gas,² we have now studied the hydroformylation reaction at low partial pressures of hydrogen and carbon monoxide.

Contrary to the prevailing opinion that increased pressure facilitates the hydroformylation reaction, our new semi-quantitative data secured with cyclohexene at 110 and 115° under widely differing $H_2:CO$ partial pressures show the following surprising results: (1) At constant carbon monoxide pressures the rate greatly increases with increasing hydrogen pressure. (2) At constant hydrogen partial pressures, the rate increases with increasing partial pressures of carbon monoxide up to about 10 atm. but decreases with higher partial pressure of carbon monoxide.

It is thus apparent that our previous observation on the independence of rate with pressure was owing to the relatively equal but opposite effects of increasing the partial pressure of the two gases, hydrogen and carbon monoxide.

Experimental.—A solution of cyclohexene and dicobalt octacarbonyl (34 g. and 1.4 g. per 100 g. of solution, respectively) in toluene was treated at $110 \pm 1^\circ$ for 68 minutes in a series of experiments under 10 atm. of CO and at various partial pressures of H_2 . When the partial pressure of H_2 was 27, 54 and 110 atm., the conversion of olefin to cy-

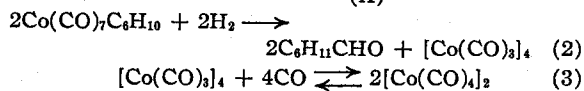
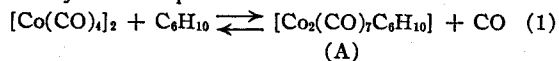
clohexanecarboxaldehyde was 30, 51, and 65%, respectively.

With 55 atm. of H_2 and under otherwise identical conditions except that the partial pressure of CO was 3, 5, 14, 28 and 54 atm., olefin conversions of 35, 46, 43, 29 and 18%, respectively, were secured.

With a constant $H_2:CO$ ratio of unity and total pressures of 53, 110 and 220 atm., the conversion of olefin was 15.3, 18 and 17.3%, respectively, again illustrating the apparent independence of rate at relatively high pressure of 1:1 gas.

When 2-ethyl-1-hexene was employed, essentially the same results as above were secured.

Discussion.—The above data may be explained if, in the initial stage of the reaction, some equilibrium is involved between a carbonyl of cobalt (possibly dicobalt octacarbonyl or the hydrocarbonyl), carbon monoxide and the olefin, the latter being able to substitute for some of the CO in the carbonyl. One possible scheme for the reaction is



It is possible that the postulated intermediate (A) is formed from the decomposition of the complex $[Co(CO)_4 \cdot olefin]^+[Co(CO)_4]^-$ recently suggested by Orchin³ but further work is required, especially since the above tentative scheme does not assign a role to the hydrocarbonyl.

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(3) M. Orchin, in "Advances in Catalysis," Vol. V, Academic Press, Inc., New York, 1953, p. 407.

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(1) G. Natta and R. Ercoli *Chimica e Industria* 34, 503 (1952).

(2) G. Natta, P. Pino and E. Mantica, *ibid.*, 32, 201 (1950).