Journal of Organometallic Chemistry, 219 (1981) 397—400
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

REACTION OF $HCo(CO)_4$ WITH OLEFINS. EFFECT OF $Co_2(CO)_8$

FERENC UNGVÁRY and LÁSZLÓ MARKÓ

Department of Organic Chemistry, University of Chemical Engineering, H-8200 Veszprém (Hungary)

(Received May 6th, 1981)

Summary

Dicobalt octacarbonyl catalyzes the formation of acylcobalt tetracarbonyls and paraffins from olefins and cobalt tetracarbonyl hydride, presumably by generating radical species. The relative reactivities of CO and $HCo(CO)_4$ towards an alkylcobalt carbonyl determine the carbonylation/hydrogenation ratio.

The reaction between $HCo(CO)_4$ and olefins is regarded as component of the hydroformylation catalytic cycle in the presence of cobalt carbonyls, and because of the industrial significance of hydroformylation it has been repeatedly studied [1]. The main products of this stoichiometric reaction are aldehydes and saturated hydrocarbons (at low olefin/$HCo(CO)_4$ ratios) or acylcobalt tetracarbonyls $RCOCo(CO)_4$ (at high olefin/$HCo(CO)_4$ ratios in the presence of CO).

By monitoring the CO absorption the rate of acylcobalt tetracarbonyl formation from two olefins, heptene-1 or octene-1 (5—50 fold excess), $HCo(CO)_4$ dissolved in heptane and CO at 15°C and 0.5—3 bar has been measured in the presence of $Co_2(CO)_8$ (eq. 1)

$$RCH{=}CH_2 + HCo(CO)_4 + CO \xrightarrow{Co_2(CO)_8} RC_2H_4COCo(CO)_4 \quad (1)$$

The reaction is half order in $Co_2(CO)_8$ and first order in olefin. The rate dependence on the $HCo(CO)_4$ and CO concentrations (CO inhibits the reaction) is more complex (see below). A significant amount of saturated hydrocarbon is formed as by-product, and since this results in the formation of additional $Co_2(CO)_8$ (eq. 2) initial rates were used to avoid autocatalytic effects.

$$RCH{=}CH_2 + 2\ HCo(CO)_4 \xrightarrow{Co_2(CO)_8} RC_2H_5 + Co_2(CO)_8 \quad (2)$$

One possible mechanism which explains the kinetic data is:

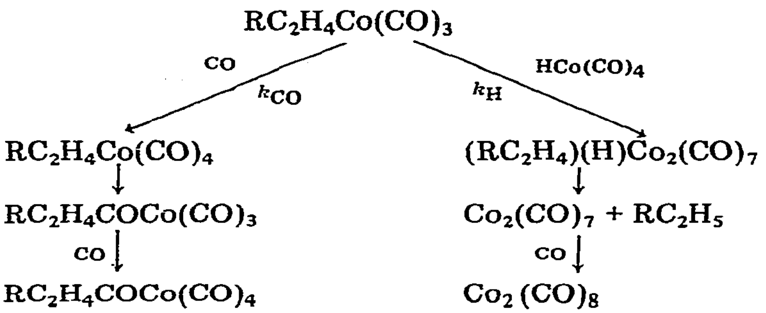
$$Co_2(CO)_8 \overset{K_1}{\rightleftharpoons} 2\ {}^{\cdot}Co(CO)_4$$

0022-328X/81/0000—0000/$02.50

$$^{\bullet}Co(CO)_4 + RCH{=}CH_2 \overset{K_2}{\rightleftharpoons} {}^{\bullet}Co(CO)_3(RCH{=}CH_2) + CO$$

$$^{\bullet}Co(CO)_3(RCH{=}CH_2) + HCo(CO)_4 \xrightarrow[\text{slow}]{k_a} HCo(CO)_3(RCH{=}CH_2) + {}^{\bullet}Co(CO)_4$$

$$HCo(CO)_3RCH{=}CH_2) \overset{K_3}{\rightleftharpoons} RC_2H_4Co(CO)_3$$



Assuming that formation of $HCo(CO)_3RCH{=}CH_2$ and reaction of $RC_2H_4Co(CO)_3$ are equal (steady state treatment), the following rate expressions can be derived for the formation of $RC_2H_4COCo(CO)_4$ (eq. 3) and RC_2H_5 (eq. 4) if $[Co_2(CO)_8]$ and $[RCH{=}CH_2]$ are constant:

$$\frac{d[RC_2H_4COCo(CO)_4]}{dt} = r_{CO} = \frac{B\dfrac{k_{CO}}{k_H}[HCo(CO)_4]}{\dfrac{k_{CO}}{k_H}[CO] + [HCo(CO)_4]} \qquad (3)$$

$$\frac{d[RC_2H_5]}{dt} = r_H = \frac{B[HCo(CO)_4]^2[CO]^{-1}}{\dfrac{k_{CO}}{k_H}[CO] + [HCo(CO)_4]} \qquad (4)$$

where $B = A[Co_2(CO)_8]^{0.5}[RCH{=}CH_2]$ and $A = k_a K_1^{0.5} K_2$.

The kinetic constants A and (k_{CO}/k_H) may be determined by transforming eq. 3 into eq. 5.

$$\frac{1}{r_{CO}} = \frac{[CO]}{B[HCo(CO)_4]} + \frac{1}{B\dfrac{k_{CO}}{k_H}} \qquad (5)$$

and plotting $(1/r_{CO})$ against $([CO]/[HCo(CO)_4])$. This is shown in Fig. 1 for the two olefins.

The following (k_{CO}/k_H) and A values were obtained:

	$\frac{k_{CO}}{k_H}$	$A \times 10^3$ ($mol^{-0.5}\ l^{0.5}\ min^{-1}$)
Heptene-1	9.6	2.0
Octene-1	7.8	1.8

Using the values for octene-1, values of r_H have been calculated from eq. 4 and compared with those determined by measuring the amount of octane

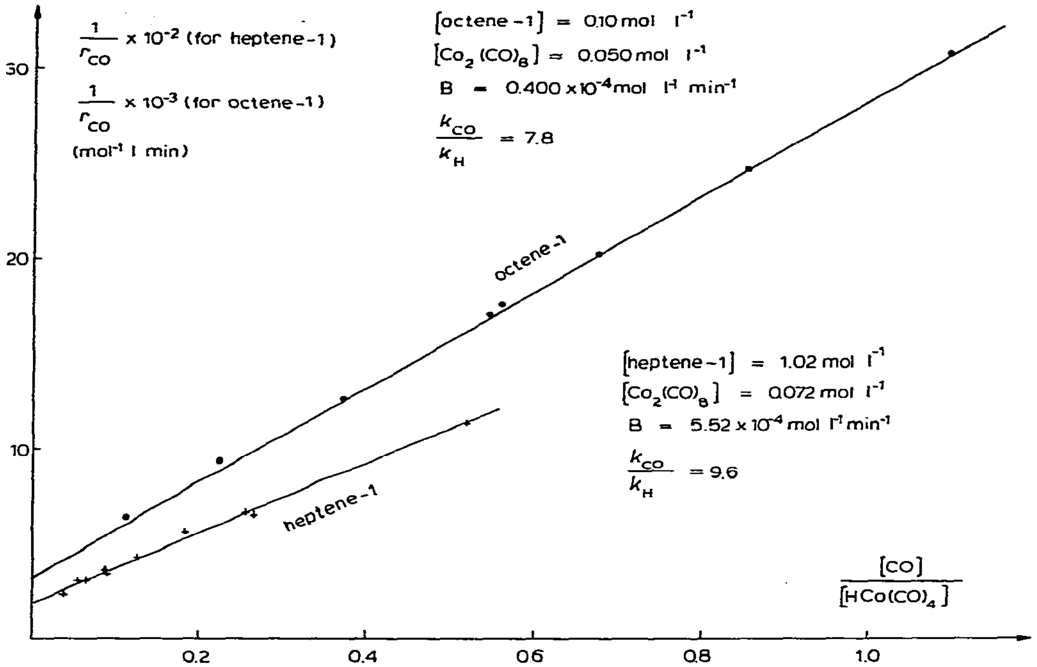


Fig. 1. The reciprocal initial rate of CO absorption ($1/r_{CO}$) vs. ($[CO]/[HCo(CO)_4]$) at 15°C in heptane solution under CO between 0.5 and 3 bar total pressure in the presence of $Co_2(CO)_8$ for octene-1 (●) and for heptene-1 (+).

formed directly by GLC. The reasonable agreement between the calculated and measured r_H values is shown in Fig. 2.

The mechanism proposed is obviously not the only one which fits the kinetic

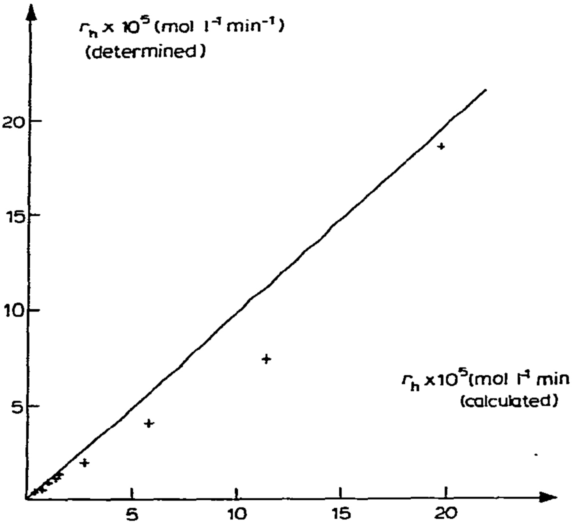


Fig. 2. Comparison of the experimental and calculated initial rates of hydrogenation (r_H) for octene-1.

data, but at the present level of knowledge further speculation is unwarranted. It is important to note the apparently general catalytic role of $Co_2(CO)_8$ in these reactions of $HCo(CO)_4$ [2,3] which require the loss of a CO ligand from $HCo(CO)_4$. Obviously, more work is needed to determine the exact way by which $Co_2(CO)_8$ exerts its influence.

Our experiments provide quantitative support for the widely accepted conclusion from qualitative studies of both catalytic and stoichiometric hydroformylations that the ratio of hydrogenation to carbonylation increases with the $HCo(CO)_4$ concentration and decreases with the CO concentration, and explain this effect in terms of the competing reactions of CO and $HCo(CO)_4$ with the intermediate alkylcobalt tricarbonyl.

Preliminary experiments indicate a different kinetic picture for styrene as olefin; the results will be reported later.

References

1 P. Pino, F. Piacenti and M. Bianchi, Reactions of Carbon Monoxide and Hydrogen with Olefinic Substrates; The Hydroformylation (OXO) Reaction, in I. Wender and P. Pino (Eds.), Organic Synthesis via Metal Carbonyls, Vol. 2, J. Wiley, New York, 1977, pp. 43—135.

2 J. Csizmadia, F. Ungváry and L. Markó, Trans. Metal. Chem., 1 (1976) 170.

3 A.C. Clark, J.F. Terapane, Jr. and M. Orchin, J. Org. Chem., 39 (1974) 2405; R.W. Wegman and T.L. Brown, J. Amer. Chem. Soc., 102 (1980) 2494; F. Ungváry and L. Markó, J. Organometal. Chem., 193 (1980) 383.