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Mechanism of Hydroformylation, Part II†

Study of the Formation of Hydrocobalttetracarbonyl by the Reaction of $Co_2(CO)_8$ and H_2

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With 8 Figures

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The kinetics and the position of the equilibrium of the reaction $Co_2(CO)_8 + H_2 \rightleftarrows 2\ HCo(CO)_4$ were studied in the range of 80–160 °C and 50–100 atm. by means of in situ IR spectroscopy.

The reaction is reversible first order with respect to $Co_2(CO)_8$ and $HCo(CO)_4$ and the energies of activation of the forward and the reverse reaction are found to be 17,3 cal/mole, and 11.0 kcal/mole resp.

The reaction is slightly endothermic with $\Delta H = 6.6$ kcal/mole and $\Delta S = 14.6$ e.u. The heat of formation of $HCo(CO)_4$ and the bond strength between hydrogen and cobalt in $HCo(CO)_4$ were found to be — 146.1 kcal/mole and 54.7 kcal/mole resp.

Introduction

The hydroformylation reaction is the synthesis of aldehydes from olefins and synthesis gas in the presence of the cobalt carbonyl catalyst at 75–200 °C and 100–300 atm.[1]. Under the reaction conditions and in the absence of olefin any form of cobalt is converted into $Co_2(CO)_8$ and $HCo(CO)_4$[2].

Since hydroformylation[3] is dependent upon the active species

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† Part I see Ref. [13].

$HCo(CO)_4$ rather than on $Co_2(CO)_8$, it was of utmost importance to study the position of equilibrium and kinetics of.

$$Co_2(CO)_8 + H_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\ HCo(CO)_4 \qquad (I)$$

The kinetics at a single temperature were studied before by *Iwanaga*[4] and equilibrium studies were done by *Gankin* et al.[5] and *Ungváry*[6]. In all these papers the concentrations of $Co_2(CO)_8$ and $HCo(CO)_4$ were determined indirectly at ambient temperatures and pressures from the samples recovered from the autoclave. This could lead to serious misinterpretation due to the reaction taking place on sampling. The necessity was felt for an analytical means which enabled the measurements of the above mentioned components to be performed under truely in situ conditions; for this a high pressure—high temperature IR spectroscopic cell was developed[7].

Using this apparatus, the $Co_2(CO)_8$—P*Bu*$_3$ catalyst system under synthesis gas has been studied and already reported from this laboratory[8]. Due to the importance of the reaction (I) in hydroformylation and also for $Co_2(CO)_8$—P*Bu*$_3$ system further study was continued on the $Co_2(CO)_8$—$HCo(CO)_4$ interchange.

Results

Calibration of the Method

$Co_2(CO)_8$ (0.28 g) was dissolved in heptane (400 cm^3), charged into the autoclave and pressurized with CO. The IR spectra of a sample under CO pressure, gave the characteristic absorption bands of $Co_2(CO)_8$: 2068 (v. s.), 2041 (v. s.), 2024 (v. s.) and 1860 (m) cm^{-1} [9]. These absorption bands have also been observed at 1 atm. (Fig. 1).

At constant temperature, the absorbances of the bands of $Co_2(CO)_8$ were correlated with the concentration of $Co_2(CO)_8$ in the solution. These obeyed *Beer's* Law and with this law the absorptivities of the different absorption bands were determined. By increase of the system temperature the absorption bands did not shift, but the absorptivities of the bands decreased (Fig. 2).

By introduction of H_2 to the system an IR spectrum as shown in Fig. 3 was obtained.

The absorbance of $Co_2(CO)_8$ at 2068 cm^{-1} decreased and the absorbances of the bands at 2055 and 2032 cm^{-1} increased. The latter bands are due to $HCo(CO)_4$.

The absorptivity of $HCo(CO)_4$ is determined at high pressure and temperatures using the additivity rule of absorbances, since $Co_2(CO)_8$ has also an absorption band in $HCo(CO)_4$ region.

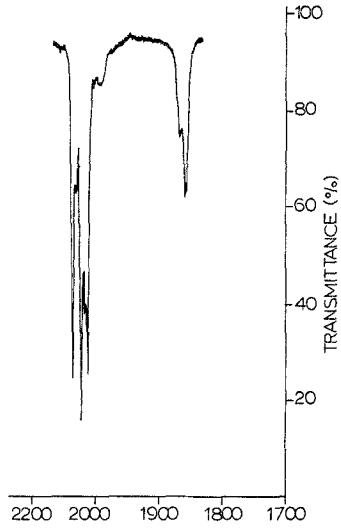

Fig. 1. Infrared Spectrum of $Co_2(CO)_8$ at 1 atm CO and 25 °C

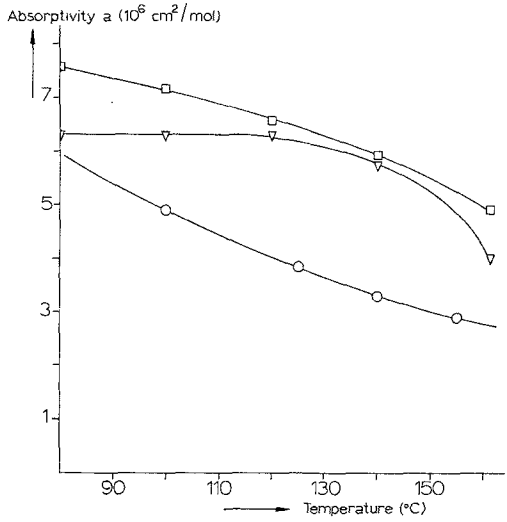

Fig. 2. Influence of temperature on the absorptivities of $Co_2(CO)_8$ absorptions at 1068 cm^{-1} ▽, 2024 cm^{-1} □ and $HCo(CO)_4$ absorption at 2,032 cm^{-1} ○

The amount of cobalt that is in the form of $HCo(CO)_4$ was obtained as the difference between the total amount of cobalt charged and the amount of $Co_2(CO)_8$ (from its absorption band at 2068 cm^{-1}). This

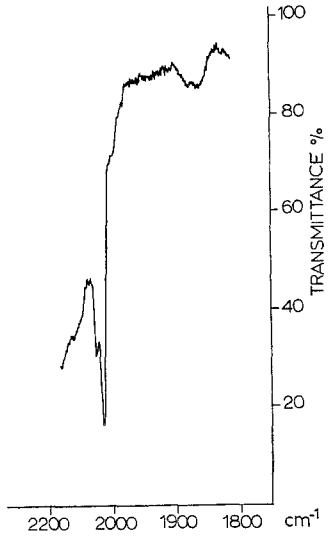

Fig. 3. Infrared Spectrum of the equilibrium mixture of $Co_2(CO)_8$ and $HCo(CO)_4$ at 125 °C $P_{CO} = P_{H_2} = 50$ atm.

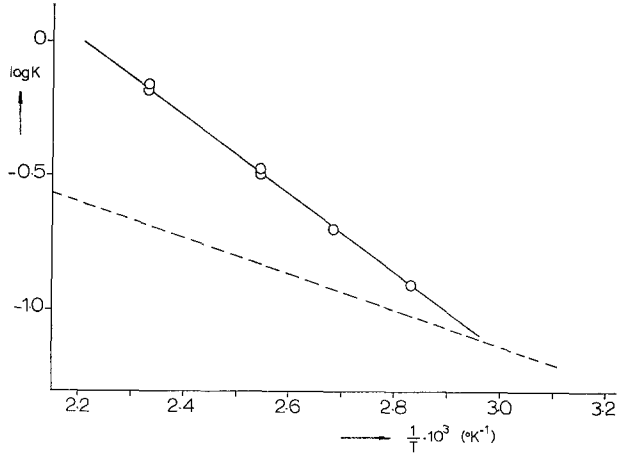

Fig. 4. Influence of temperature on the equilibrium constant of reaction (I). Full line: present work. Dotted line *Ungváry* [6]

technique allowed the determination of the concentration of $CO_2(CO)_8$ and $HCo(CO)_4$ at reaction conditions within an error of 4%.

The solubilities of H_2 and CO in heptane were determined separately

in a 5 litres autoclave in the range of temperature and pressures of the prevailing study. The results did not show a significant deviation from the extrapolated literature data[6].

Equilibrium Study

The equilibrium study of reaction (I) was started by the addition of H_2 to the solution of $Co_2(CO)_8$ in heptane under CO pressure. Time was given for the equilibrium to be attained. This went up to 60 hrs. at temperatures below 100 °C. The intensity of mixing the partial pressures of CO and H_2, and the temperatures were held constant during the time of approach to the equilibrium.

The equilibrium constants calculated as a function of temperatures are listed in the following table.

Table 1. *Equilibrium Constant of Reaction* $Co_2(CO)_8 + H_2 \rightleftharpoons 2\,HCo(CO)_4$

$$K = \frac{[HCo(CO)_4]^2}{[Co_2(CO)]_8\,[H_2]}$$

Temp., °C	$Co_2(CO)_8$ mmol/l	$HCo(CO)_4$ mmol/l	H_2 mmol/l	K	log K
80	0.731	2.52	70	0.124	— 0.906
100	0.651	3.08	72	0.202	— 0.695
120	0.584	3.74	75	0.319	— 0.496
	0.566	3.78	75	0.337	— 0.472
155	0.326	4.255	85	0.653	— 0.185
	0.316	4.276	85	0.681	— 0.167
	0.324	4.26	85	0.659	— 0.181

The plot of log K versus $1/T$ is given in Fig. 4.

For a comparison the data of *Ungváry*[6] are plotted as the dotted line. The thermodynamic parameters were derived therefrom as $\Delta H = 6.6$ kcal/mole and $\Delta S = 14.6$ e. u.

The heat of formation of $HCo(CO)_4$ is estimated as —146.1 kcal/mole from ΔH of reaction and ΔH_f of $Co_2(CO)_8$ —298.8 kcal/mole as given in literature[10]. The bond strength of H—Co was calculated using the bond enthalpies of the bonds of Co—Co, 12 kcal/mole[10, 11], and of H_2, 104 kcal/mole[12] and ΔH of reaction. This resulted in a H—Co bond strength of 54.7 kcal/mole.

Kinetic Study

The rate of formation of $HCo(CO)_4$ was followed at different temperatures. All reaction rates were determined at conditions where the diffusional effects were eliminated. This was achieved at an impeller speed higher than that of 900 r. p. m. As an example the measurements at 100 °C are presented in Fig. 5.

The data did not correlate with an irreversible first order equation

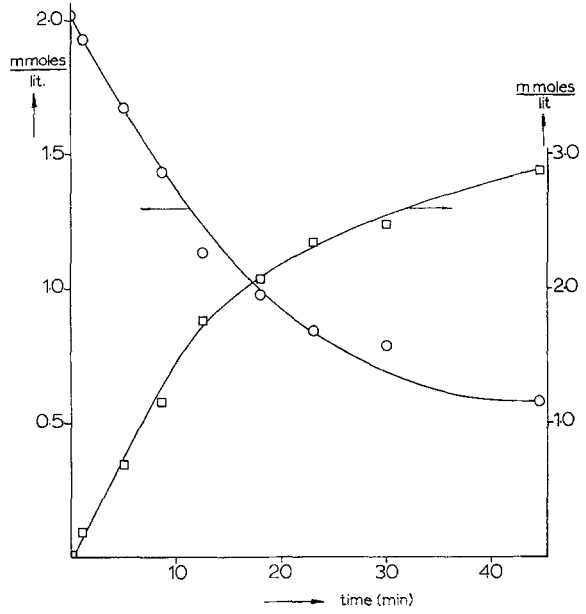

Fig. 5. $Co_2(CO)_8$—$HCo(CO)_4$ interchange as a function of time. ○ $Co_2(CO)_8$ □ $HCo(CO)_4$ 100 °C, $P_{CO} = P_{H_2} = 25$ atm. $Co_2(CO)_8$ 2.04 mmol/l at zero time

(Fig. 6), but fitted excellently to a reversible kinetic equation for conversion levels of up to 85%.

This can be seen from the plot of ln $(C_A - C_{Ae})/(C_{Ao} - C_{Ae})$ versus time; C_{Ag} stands for the equilibrium concentration which was found from Fig. 4. The slope of the line is equal to $k_1\,(1 + 1/K)$ and from this the forward (k_1) and the reverse (k_2) reaction rate constants were evaluated to be 8.78×10^{-3} min^{-1} and 4.25×10^{-2} min^{-1} resp. at 100 °C.

The *Arrhenius* plot gave a linear line for both the forward and reverse reaction rate constants (Fig. 7), so that the energies of activation are as follows: for the forward reaction 17.3 kcal/mole and for the reverse eaction 11.0 kcal/mole.

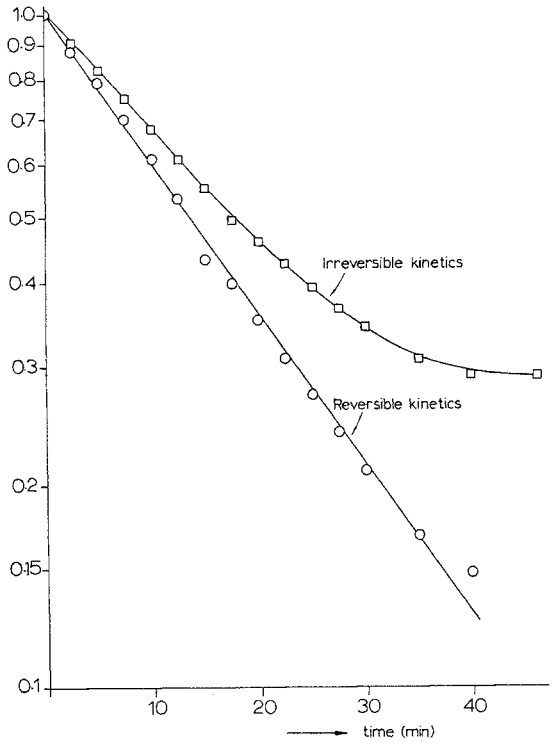

Fig. 6. Plot of ln C_A/C_{Ao} and $\ln(C_A-C_{Ae})/C_{Ao}-C_{Ae})$ versus time for reaction (I) 100 °C, $P_{CO} = P_{H_2} = 25$ atm. $Co_2(CO)_8$ 2.04 mmol/l at zero time

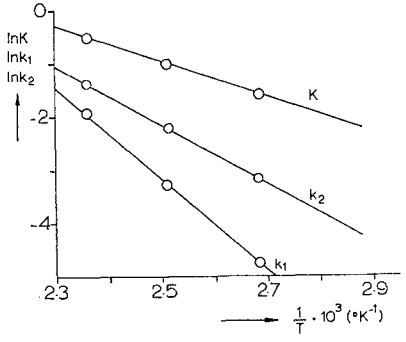

Fig. 7. Influence of the temperature on the forward (k_1) and the reverse (k_2) reaction rate constant and the equilibrium constant K

Discussion

Comparison of our results with those presented by *Ungváry*[6] is as follows:

		Ungváry	Ours
ΔH	kcal/mole	3.2	6.6
ΔS	e.u.	4.4	14.6
ΔH_f	kcal/mole	—	— 146.1
ΔH (H—Co)	kcal/mole	58	54.7

In the range of temperatures covered in our study (80–160 °C) the free energy of the reaction showed a smaller positive value than the previous results, which means that the reaction is nonspontaneous, but the potentiality for the reaction is higher than the earlier estimates.

The comparison of the kinetic results with those reported by *Iwanaga*[4] at 100 °C showed that the rate of the reaction found in this work is three times faster under the same conditions of the reaction.

The difference between the present and the earlier reports on kinetics and equilibrium can be attributed to the experimental technique. The concentrations of the components in this work are determined under truely in situ conditions. But the existing data in literature were collected from the samples obtained from the autoclave, which is cooled and analyzed by indirect techniques (acid-base titration). The reactions that take place during the sampling alter the concentration of the components so that the concentrations obtained by sampling are not representative of the concentrations of the components in the autoclave. We have noticed that the conversion to $HCo(CO)_4$ was lower with a cold sample line than with a sample line controlled at the same temperature of the autoclave and the cell. This is due to the fact that the reaction is reversible first order and the reverse reaction rate constant is higher than the forward reaction rate constant (see Fig. 7). Therefore the results obtained by sampling leads to lower conversions, thus lower rate and equilibrium constants.

The difference between the heat of reaction found by equilibrium studies and the heat of reaction estimated by the difference between the activation energy of the forward and the reverse reaction is 0.3 kcal/mole. This insignificant difference may arise by the accumulation of errors.

Our studies suggest that due to the endothermicity of the reaction, higher temperatures should be used. These give higher rate of formation and equilibrium concentration of $HCo(CO)_4$, which requires higher partial pressures of CO, that is essential for the stability of the carbonyls[13].

Experimental

High Temperature/High Pressure Infrared Cell Assembly

The assembly consists of a high pressure injection port of 45 cm^3, an high pressure/high temp. infrared cell which are connected to a 1 litre 316 stainless steel autoclave equipped with impeller type stirrer, Fig. 8.

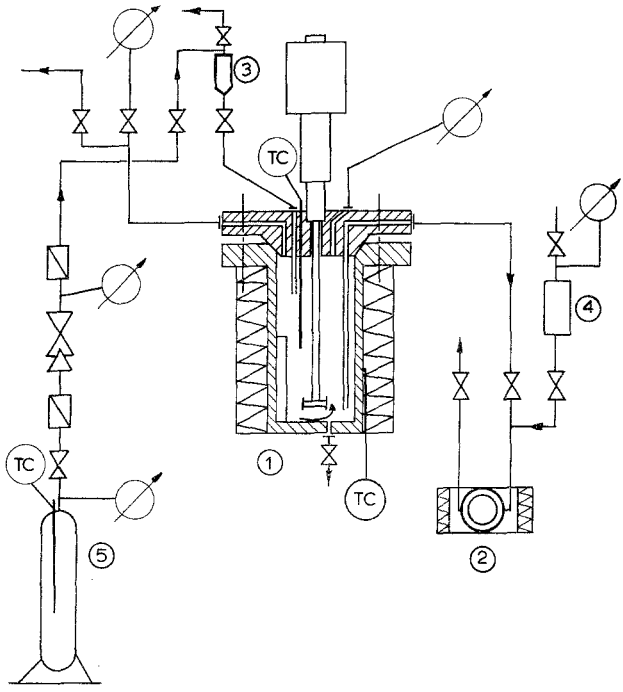

Fig. 8. High temperature/high pressure Infrared cell assembly. 1. 1 litre stainless steel 316 autoclave. 2. The high temperature/high pressure infrared cell. 3. 45 cm^3 high pressure injection port. 4. Cell cleaning unit. 5. 10 litre high pressure CO and H_2 tanks

Solution of $Co_2(CO)_8$ ($\approx$ 0.28 g) in heptane ($\approx$ 400 cm^3) is sucked into the autoclave by vacuum. After purging the system with CO it is pressurized under vigorous stirring. The autoclave, the cell and the sample line are brought to the reaction temperature.

In cases where it is necessary to increase the concentration of $Co_2(CO)_8$ (e.g. for the determination of absorptivity), the injection port is filled with a known quantity of $Co_2(CO)_8$ dissolved in 40 cm^3 heptane. After purging with CO it is injected into the autoclave by a pressure difference.

The reaction is started with the addition of H_2 to the system. The pressure of the system is regulated within 1 atm. with a regulating valve supplied by Volumetric Inglewood California.

After stopping the stirring, the samples from the autoclave contents are transferred to the cell by slowly opening a high pressure valve downstream of the cell, so that the confined sample always remains at the same temperature and pressure. The spectra of samples are recorded with the infrared spectrophotometer (Perkin Elmer 357 Grating type) with heptane in CaF_2 windows serving as reference.

The temperatures are measured by calibrated chromel-alumel thermocouples in the center of autoclave, its wall and the sample line. The temperature of the autoclave content is regulated within 1 °C by Eurotherm PID controller, which is affectuated by the temperature of the autoclave wall. The temperature of the cell and the sample line are regulated separately and hand controlled.

All parts of the apparatus and the lines are made of stainless steel.

Preparation of $Co_2(CO)_8$

Both high temperature/high pressure preparative techniques of *Wender* et al. [14] and *Markó* et al. [15] have been applied.

CO evolution [16] and cobalt analysis [17]* on the product after several recrystallizations have proved the superiority of *Markó's* process. A maximum of 94% purity is achieved with the former preparative technique, while with the latter one a purity as high as 99% is obtained. *Markó's* method, with a slight modification of the recrystallization, was therefore preferred.

Recrystallisation was done by dissolving the raw product in CH_2Cl_2 to the saturation level at 20 °C cooling to — 30 °C for 1 day and filtering of the recrystallized product. All operations were carried out under CO atmosphere. The chemicals were supplied by Baker (heptane, cobalt acetate tetrahydrate and dichloromethane).

CO was delivered by Hoek and Loos, and H_2 by Holtz and Co., Hamburg, with a 99% purity.

The hydrogen was dried over molecular sieves and passed through a De-oxo-D (0.5% Pd on Al_2O_3) catalyst prior to use.

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* The cobalt in $Co_2(CO)_8$ is oxidized to Co^{2+} (in a boiling solution of concentrated HNO_3 and a few drops of H_2O_2). From there on the procedure of *Kolthoff* and *Elvin* [17] is followed.

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