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KINETICS AND EQUILIBRIUM OF $Co_2(CO)_6(\eta^4$-norbornadiene) FORMATION FROM $Co_2(CO)_8$ AND NORBORNADIENE UNDER CO *

FERENC UNGVÁRY, JABIR SHANSHOOL ** and LÁSZLÓ MARKÓ
Institute of Organic Chemistry, University of Veszprém, 8201 Veszprém (Hungary)

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Summary

The formation of $Co_2(CO)_6(\eta^4\text{-NBD})$ from $Co_2(CO)_8$ and NBD is a reversible endothermic reaction:

$$Co_2(CO)_8 + NBD \underset{k_{-CO}}{\overset{k_{CO}}{\rightleftharpoons}} Co_2(CO)_6(\eta^4\text{-NBD}) + 2CO;$$

ΔH^0 14.9 ± 0.7 kcal mol^{-1}

In the forward reaction the carbon monoxide evolution is of first order in both $Co_2(CO)_8$ and NBD and of minus first order in CO. The carbon monoxide uptake in the reverse reaction is first order in both $Co_2(CO)_6(\eta^4\text{-NBD})$ and CO. The temperature dependence of the equilibrium constant K, and of the rate constant for the forward reaction k_{CO} between 25 and 45°C is represented by $\log_{10} K = (7.41 \pm 0.48) - (3259 \pm 147)/T$ (K in M) and $\log_{10} k_{CO} = (18.30 \pm 1.75) - (7054 \pm 540)/T$ (k_{CO} in s^{-1}).

Introduction

Olefin complexes of cobalt carbonyls may play an important role in homogeneous hydroformylation, hydrogenation and isomerization of olefins, but very little is known about the mechanism of formation and the chemistry of such complexes [1].

Dicobalt octacarbonyl reacts with dienes in boiling hydrocarbon solvents to give $Co_2(CO)_6(\eta^4\text{-diene})$ and $Co_2(CO)_4(\eta^4\text{-diene})_2$ complexes in a ratio depending on the ratio of reactants and the temperature [2]. To obtain quantitative kinetic and thermodynamic information about this olefin complex formation we have made a kinetic study of reaction 1 (NBD = norbornadiene; bicyclo[2.2.1] hepta-1,5-diene):

$$\underset{(1)}{Co_2(CO)_8} + \underset{(2)}{NBD} \underset{k_{-CO}}{\overset{k_{CO}}{\rightleftharpoons}} \underset{(3)}{Co_2(CO)_6(\eta^4\text{-NBD})} + 2\ CO \tag{1}$$

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Results and discussion

Reactants **1** and **2** react smoothly near room temperature to reach the equilibrium shown in eq. 1. The rates of the forward and reverse reactions were determined by observing the change in carbon monoxide volume in a thermostatted gasometric apparatus at constant pressure. The formation of tetracobalt dodecacarbonyl (**4**) (eq. 2) is at least two orders of magnitude slower at 35°C [3] and so its influence on the initial rate of CO evolution in the presence of **2** can be neglected.

$$2\ Co_2(CO)_8 \rightarrow Co_4(CO)_{12} + 4\ CO \qquad (2)$$

This was confirmed by the observation that when the change in the CO volume had ceased no $Co_2(CO)_4(\eta^4\text{-NBD})_2$ [2a,b] nor $Co_4(CO)_{12}$ [4] could be detected by their characteristic absorptions in the infrared spectra.

The equilibrium concentrations of the species involved in reaction 1 could be calculated either from the maxima of the CO evolution or from the infrared spectra of the equilibrium mixtures using the known absorptions for **1** [5] and for **3** (see experimental part). There was good agreement between the K values calculated by the two methods.

TABLE 1

INITIAL RATES OF CO EVOLUTION (r_{CO}), THE MAXIMA OF EVOLVED CO (CO_{max}), THE OBSERVED RATE CONSTANTS ($k_{CO} = r_{CO}[CO]/[\mathbf{1}][\mathbf{2}]$) AND THE EQUILIBRIUM CONSTANTS ($K = [\mathbf{3}][CO]^2/[\mathbf{1}][\mathbf{2}]$) FOR THE REACTION OF **1** WITH **2** UNDER CO IN n-OCTANE SOLUTION UNDER VARIOUS CONDITIONS

Temperature (°C)	[**1**] (M)	10^2[CO] [a] (M)	[**2**] (M)	$10^6 r_{CO}$ ($M\ s^{-1}$)	CO_{max} [b] (%)	$10^5 k_{CO}$ (s^{-1})	$10^5 K$ [c] (M)
20	0.098	1.13	0.463	6.6	–	0.15	–
25	0.040	1.15	0.463	8.0	52.4	0.43	3.0
30	0.040	1.17	0.463	16.0	59.0	1.02	4.4
35	0.010	1.20	0.185	3.7	44.0	2.4	6.3
35	0.020	0.59	0.185	15.7	76.3	2.5	6.6
35	0.020	1.17	0.185	7.4	44.8	2.3	6.4
35	0.040	0.59	0.093	15.7	54.4	2.5	6.0
35	0.040	1.20	0.093	8.0	27.0	2.4	6.6
35	0.040	1.19	0.185	15.8	43.3	2.4	6.6
35	0.040	2.60	0.185	7.2	14.3	2.3	6.3
35	0.040	3.40	0.185	4.3	10.0	2.0	7.0
35	0.040	1.16	0.464	35.0	–	2.2	–
35	0.040	3.17	0.463	11.3	21.9	1.9	6.2
35	0.040	1.16	0.927	67.8	82.8	2.1	7.1
35	0.098	1.19	0.185	34.1	40.3	2.2	6.6
35	0.194	1.18	0.185	61.2	31.7 [d]	2.0	(5.3)
35	0.194	1.18	0.000	0.31 [e]			
40	0.020	1.23	0.185	17.6	51.6	5.8	10.0
45	0.020	1.24	0.093	20.1	43.8	13.5	14.6

[a] Calculated from $p(CO)$ and the solubility of CO in n-octane. [b] Percentage values calculated on the basis of reaction 1. [c] Calculated in two ways, one using the CO_{max} values and the other, the equilibrium concentrations of **1** and **3** as measured by infrared spectroscopy. Agreement within 10% was found and average values are listed. [d] **3** partially crystallized from the solution towards the end of the reaction. [e] A value of $0.30 \times 10^{-6}\ M\ s^{-1}$ can be calculated using literature data for reaction 2 [3].

TABLE 2

INITIAL RATES OF CO ABSORPTION ($r_{-\mathrm{CO}}$), THE MAXIMA OF ABSORBED CO ($-\mathrm{CO}_{\mathrm{max}}$), THE OBSERVED RATE CONSTANTS ($k_{-\mathrm{CO}} = r_{-\mathrm{CO}}/[3][\mathrm{CO}]$) AND THE EQUILIBRIUM CONSTANTS ($K = [3][\mathrm{CO}]^2/[1][2]$) FOR THE REACTION OF 3 WITH CO IN n-OCTANE SOLUTION AT 35°C

[3] (M)	10^2[CO] [a] (M)	[2] (M)	$10^6 r_{-\mathrm{CO}}$ ($M\ \mathrm{s}^{-1}$)	$-\mathrm{CO}_{\mathrm{max}}$ [b] (%)	$10^2 k_{-\mathrm{CO}}$ ($M^{-1}\ \mathrm{s}^{-1}$)	$10^4 K$ [c] (M)	$10^4 K$ [d] (M)
0.057	1.20	0.051	23.2	69.4	3.4	7.0	5.9
0.031	1.20	0.051	13.0	71.4	3.5	7.9	6.5
0.033	1.20	0.000	16.2	[e]	4.0	–	6.7
0.034	0.40	0.051	5.1	25.1	3.6	7.6	6.6
0.013	1.20	0.000	6.0	[e]	3.8	–	8.2

[a] Calculated from p(CO) and the solubility of CO in n-octane. [b] Percentage values calculated on the basis of reaction 1. [c] Calculated using the equilibrium concentrations derived from the $-\mathrm{CO}_{\mathrm{max}}$ values. [d] Calculated using the equilibrium concentrations of **1** and **3** measured by infrared spectroscopy. [e] Not measured.

The experimental results and the calculated rate and equilibrium constants are listed in Table 1 and Table 2. The average value of the equilibrium constant K at 35°C, calculated from the equilibrium concentrations in the experiments ($K = [\mathrm{Co_2(CO)_6(\eta^4\text{-}NBD)}][\mathrm{CO}]^2/[\mathrm{Co_2(CO)_8}][\mathrm{NBD}] = 6.7 \pm 0.4 \times 10^{-4}\ M$) shows excellent agreement with the value calculated from the ratio of the rate constants for the forward and reverse reactions $K = k_{\mathrm{CO}}/k_{-\mathrm{CO}} = 2.3 \pm 0.2 \times 10^{-5}\ \mathrm{s}^{-1}/3.6 \pm 0.2 \times 10^{-2}\ M^{-1}\ \mathrm{s}^{-1} = 6.4 \pm 0.9 \times 10^{-4}\ M$.

As can be seen from the data in Table 1, the forward reaction in eq. 1 is endothermic, increase in temperature shifting the equilibrium to the right hand side.

The forward reaction, starting from **1**, is first order in both **1** and **2** and minus first order in CO (Table 1). The reverse reaction, starting from **3**, is first order in both **3** and CO (Table 2).

Linear least squares fits yield eq. 3 and 4 for the temperature dependence of k_{CO} and K between 25 and 45°C (deviations represent 95% confidence level)

$$\log_{10} k_{\mathrm{CO}} = (18.30 \pm 1.75) - (7054 \pm 540)/T \qquad (3)$$

$$\log_{10} K = (7.41 \pm 0.48) - (3259 \pm 147)/T \qquad (4)$$

From these the activation energy $E_{\mathrm{a}} = 32.3 \pm 2.5$ kcal mol^{-1}, the enthalpy $\Delta H^0 = 14.9 \pm 0.7$ kcal mol^{-1} and the entropy $\Delta S^0 = 33.9 \pm 2.2$ cal mol^{-1} K^{-1} can be derived for reaction 1. Based on these data ΔG^0 would be zero at 167°C.

The kinetic behavior suggests the mechanism depicted in Scheme 1:

$$\mathrm{Co_2(CO)_8} \underset{\text{very fast}}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{Co_2(CO)_7 + CO}$$

$$\mathrm{Co_2(CO)_7 + NBD} \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} \mathrm{Co_2(CO)_7(\eta^2\text{-}NBD)}$$

$$\mathrm{Co_2(CO)_7(\eta^2\text{-}NBD)} \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{Co_2(CO)_6(\eta^2\text{-}NBD) + CO}$$

$$\mathrm{Co_2(CO)_6(\eta^2\text{-}NBD)} \underset{\text{fast}}{\overset{\text{very fast}}{\rightleftharpoons}} \mathrm{Co_2(CO)_6(\eta^4\text{-}NBD)}$$

SCHEME 1

TABLE 3

INITIAL RATES OF CO EVOLUTION (r_{CO}), THE MAXIMUM OF EVOLVED CO (CO_{max}), THE OBSERVED RATE CONSTANTS ($k_{CO} = r_{CO}[CO]/[\mathbf{1}][diene]$) AND THE EQUILIBRIUM CONSTANTS ($K = [Co_2(CO)_6(\eta^4\text{-diene})][CO]^2/[\mathbf{1}][diene]$) FOR THE REACTION OF **1** WITH DIFFERENT DIOLEFINS UNDER CO IN n-OCTANE SOLUTION AT 35°C

[**1**] (*M*)	10^2[CO] [a] (*M*)	Diene	[diene] (*M*)	$10^6 r_{CO}$ ($M\ s^{-1}$)	CO_{max} [b] (%)	$10^6 k_{CO}$ (s^{-1})	$10^4 K$ [c] (*M*)
0.080	0.88	Isoprene	1.11	35.7	30.6	0.35	0.35
0.040	1.17	2,3-Dimethyl-1,3-butadiene	0.186	0.7	11.2	1.10	0.52
0.080	1.17	2,3-Dimethyl-1,3-butadiene	0.372	2.3	13.9	0.90	0.61
0.080	1.10	2,3-Dimethyl-1,3-butadiene	1.11	8.6	32.9	1.06	0.55
0.040	1.18	1,3-Cyclohexadiene	0.185	1.7	3.3	2.71	0.26
0.080	1.12	1,3-Cyclohexadiene	1.11	21.2	18.2	2.67	0.25
0.040	1.16	Norbornadiene	0.185	16.5	43.5	25.7	6.6
0.080	1.11	1,4-Cyclohexadiene	1.11	< 0.5			

[a] Calculated from p_{CO} and the solubility of CO in n-octane. [b] Percentage values calculated on the basis of reaction 1. [c] Calculated on the basis of the CO_{max} values.

Probably the coordinatively unsaturated $Co_2(CO)_7$ and $Co_2(CO)_6(\eta^2\text{-NBD})$ formed in very low concentrations in fast preequilibria are involved in the rate-determining steps of the forward and reverse reaction, respectively.

Comparison of the rates and the equilibria for various dienes (Table 3) show quantitatively that **2** is not only the most reactive diene but also gives the most stable diene complex, in accordance with earlier qualitative observations [2].

The substitution of one coordinated CO ligand by an olefin is a thermodynamically unfavorable process [6] and so cannot usually take place in a thermal reaction. The simultaneous substitution of two (or more) C=C double bonds, however, is accompanied by a large positive entropy change, and despite being endothermic such a reaction may thus become thermodynamically favorable at higher temperatures. This is actually the situation for reaction 1, and so complexes of the type $Co_2(CO)_6$(diene) may be prepared from $Co_2(CO)_8$ in a straightforward manner.

Experimental

Materials. Commercial n-octane, norbornadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-cyclohexadiene and 1,4-cyclohexadiene were dried by standard methods and were freshly distilled under CO. Dicobalt octacarbonyl was recrystallized first from CH_2Cl_2 and then from n-heptane, in both cases under CO. The molar absorbance ($\epsilon_M(Co_2(CO)_6(\eta^4\text{-NBD}))$ at 1834 cm^{-1} (4320 ± 160 M^{-1} cm^{-1}), was determined for an n-octane solution under CO in the presence of a three fold molar excess of free **2** at 25°C. $Co_2(CO)_6$ (norbornadiene) was prepared as previously described [2c].

Kinetic runs were performed in a gasometric apparatus fitted with a mercury-filled gas burette [7]. The reactions were started in a pure CO atmosphere by injecting the diene to vigorously stirred solutions of $Co_2(CO)_8$, or, in the case of the reverse reaction, by injecting the thermostatted solvent onto solid **3**. The gas volume changes were monitored throughout and when there was no further change samples were taken for infrared spectra (Carl Zeiss Jena IR 75 spectrophotometer, 0.113 mm CaF_2 cuvette), and the equilibrium concentrations of **1** and **3** were calculated using the known absorptions for **1** at 1858 cm^{-1} [5] and for **3** at 1834 cm^{-1}. Initial rates were calculated from plots against time of gas volumes corrected for changes in volume due to vapor pressures observed in comparable blank experiments in which no cobalt complexes were present.

The solubility of CO in n-octane was calculated from the data in n-heptane [8] using the approximation that the solubility expressed in molar fractions is constant for different paraffinic hydrocarbons [9]. A similar approximation has been made for n-hexane [10].

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