Organometallics **1986**, *5*, 209–215

Kinetic Investigation of the Cleavage of *n*-Butyryl- or Isobutyrylcobalt Tetracarbonyl with Hydridocobalt Tetracarbonyl or Dihydrogen

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Received March 11, 1985

The acylcobalt tetracarbonyls $n\text{-}C_3H_7C(O)Co(CO)_4$ (**1**) and $i\text{-}C_3H_7C(O)Co(CO)_4$ (**2**) react with H_2 or $HCo(CO)_4$ to yield *n*-butyraldehyde and isobutyraldehyde, respectively. The reactions, which are part of the catalytic cycle in the industrially important hydroformylation of propene, go over the corresponding acylcobalt tricarbonyls as intermediates formed by CO loss. Radical pathways of aldehyde formation may be excluded. Although the rate constants of the reactions with $HCo(CO)_4$ are at 25 °C 24–34 times larger than those with H_2, under the conditions of catalytic hydroformylation (>100 °C and >100 bar H_2 + CO) the reaction with H_2 is mainly responsible for aldehyde formation because of its stronger temperature dependence and the large concentration of H_2.

Introduction

The cleavage of acylcobalt carbonyls by $HCo(CO)_4$ or by H_2 is regarded as the ultimate step of aldehyde formation in hydroformylation:[1]

$$RC(O)Co(CO)_4 + HCo(CO)_4 \rightarrow RCHO + Co_2(CO)_8 \quad (1)$$

$$RC(O)Co(CO)_4 + H_2 \rightarrow RCHO + HCo(CO)_4 \quad (2)$$

Conflicting reports have appeared in recent years regarding the relative importance of reactions 1 and 2 under catalytic conditions (>100 °C, >100 bar H_2 + CO). On the basis of high-pressure IR studies Alemdaroglu et al. claimed reaction 1 to be the principal route of aldehyde formation,[2] whereas Mirbach provided evidence for the predominant role of reaction 2.[3]

There is also some dispute over the mechanism of these reactions. In the case of R = EtO we have shown that the rate of ethyl formate formation is first order in $EtOC(O)Co(CO)_4$, first order in H_2 or $HCo(CO)_4$, and negative first order in CO. Most probably the bimolecular reaction between coordinatively unsaturated $EtOC(O)Co(CO)_3$ and the reducing agent is involved in the rate-determining step.[4] Similar kinetics were found for the cleavage of $EtOC(O)CH_2Co(CO)_4$ with H_2 or with $HCo(CO)_4$.[5] For R = $n\text{-}C_5H_{11}$ in reaction 1, however, it has been reported that contrary to earlier findings[6] the rate of aldehyde formation was not affected by CO and the reaction may be radical in character.[7]

Recently one of use developed a new way for the preparation of pure *n*-butyrylcobalt tetracarbonyl (**1**) and isobutyrylcobalt tetracarbonyl (**2**) by the fast and quantitative reaction of $HCo(CO)_4$ at −79 °C with ethylketene and dimethylketene, respectively.[8] Both complexes are believed to be intermediates in the commercially important propene hydroformylation. Using these model substances, we now studied the kinetics of their reductive cleavage by H_2 and $HCo(CO)_4$ in order to obtain information about the relative importance of reactions 1 and 2 and about their mechanism.

Results

n-Butyraldehyde and isobutyraldehyde were formed in quantitative reactions from *n*-butyrylcobalt tetracarbonyl (**1**) and isobutyrylcobalt tetracarbonyl (**2**), respectively, using either $HCo(CO)_4$ or H_2 under 0.5–3-bar total pressure of CO or CO + H_2 mixtures at 20–45 °C in *n*-heptane solution according to the stoichiometries of eq 3–6.

$$\underset{\mathbf{1}}{n\text{-PrC(O)Co(CO)}_4} + HCo(CO)_4 \xrightarrow{r_3} n\text{-PrCHO} + Co_2(CO)_8 \quad (3)$$

$$\underset{\mathbf{2}}{i\text{-PrC(O)Co(CO)}_4} + HCo(CO)_4 \xrightarrow{r_4} i\text{-PrCHO} + Co_2(CO)_8 \quad (4)$$

$$2\,n\text{-PrC(O)Co(CO)}_4 + H_2 \xrightarrow{r_5} 2\,n\text{-PrCHO} + Co_2(CO)_8 \quad (5)$$

$$2\,i\text{-PrC(O)Co(CO)}_4 + H_2 \xrightarrow{r_6} 2\,i\text{-PrCHO} + Co_2(CO)_8 \quad (6)$$

The initial rates of these reactions could be measured by infrared spectroscopy following the decrease of acyl complex concentration and by the increase of product concentration. From the results of the kinetic measurements at 25 °C (Figure 1 and Table I), reaction rates first order in **1** or **2**, approximately first order in $HCo(CO)_4$ or H_2, and approximately negative first order in CO were calculated. Both reductions showed a strong temperature dependence (Figure 2) and became faster by using $DCo(CO)_4$ and D_2 instead of $HCo(CO)_4$ and H_2, respectively (Table II).

At low concentrations of H_2 ($p_{H_2} \sim 1$ bar) no $HCo(CO)_4$ could be detected as an intermediate in reactions 5 and 6 by IR. At higher concentrations of H_2 (p_{H_2} = 50–80 bar), however, considerable amounts of $HCo(CO)_4$ accompanied the aldehyde product. Under the same conditions no $HCo(CO)_4$ could be detected in a blank experiment starting from $Co_2(CO)_8$ alone (Table III). These experiments show that aldehyde formation with H_2 occurs in two steps over

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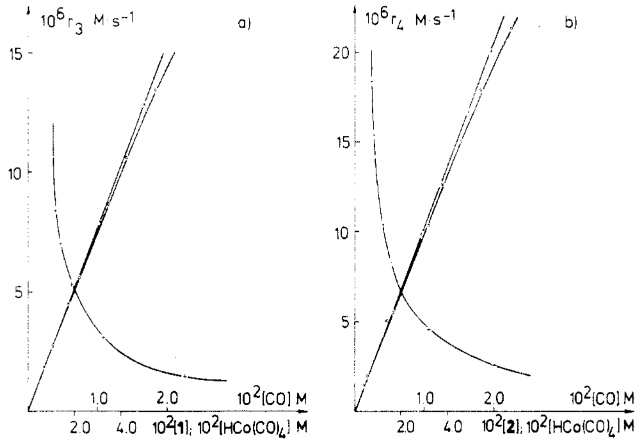


Figure 1. Influence of concentrations of initial rates of *n*-butyrylcobalt tetracarbonyl (1; r_3) and isobutyrylcobalt tetracarbonyl (2; r_4) consumption (eq 3 and 4) at 25 °C in *n*-heptane solution. a: ○, experiments at constant [1] = 0.0122 M and [CO] = 0.0108 M; ×, experiments at constant [HCo(CO)$_4$] = 0.0122 M and [CO] = 0.0108 M; +, experiments at constant [1] = [HCo(CO)$_4$] = 0.0122 M. b: ○, experiments at constant [2] = 0.0122 M and [CO] = 0.0108 M; ×, experiments at constant [HCo(CO)$_4$] = 0.0122 M and [CO] = 0.0108 M; +, experiments at constant [2] = [HCo(CO)$_4$] = 0.0122 M.

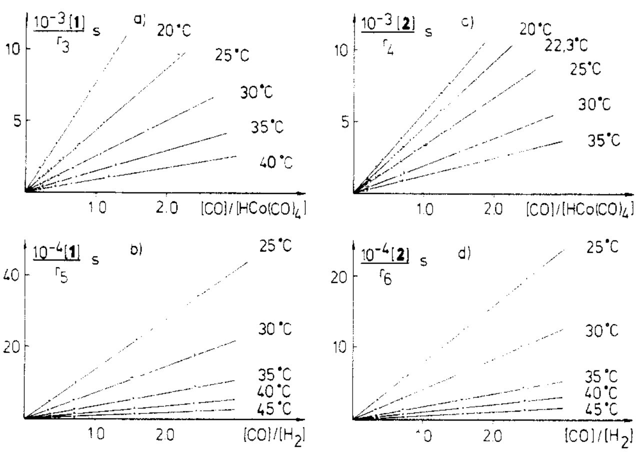


Figure 2. Kinetic data of reactions 3–6 in *n*-heptane at different temperatures plotted as [RC(O)Co(CO)$_4$]/*r* vs. [CO]/[H–X]: a, R = *n*-C_3H_7, X = Co(CO)$_4$; b, R = *n*-C_3H_7, X = H; c, R = *i*-C_3H_7, X = Co(CO)$_4$; d, R = *i*-C_3H_7, X = H.

reaction 2 followed by reaction 1, and at sufficiently high H_2 concentrations reaction 2 may become faster than reaction 1. The observed rates r_5 and r_6 are therefore at low H_2 concentrations twice as high as those of the primary reactions represented by eq 5a and 6a, respectively.

$$n\text{-PrC(O)Co(CO)}_4 + H_2 \xrightarrow{r_5'} n\text{-PrCHO} + \text{HCo(CO)}_4 \quad (5a)$$

$$i\text{-PrC(O)Co(CO)}_4 + H_2 \xrightarrow{r_6'} i\text{-PrCHO} + \text{HCo(CO)}_4 \quad (6a)$$

The data in Table III show that CO exerts its negative influence on the rates of reactions 5 and 6 not only around atmospheric pressure but also at high pressures as well.

By adding Ph_3P to solutions of 1 and 2 in *n*-heptane, 1 mol of CO was released and the Ph_3P derivatives of the acyls were formed (eq 7 and 8).

$$1 + Ph_3P \xrightarrow{r_7} n\text{-PrC(O)Co(CO)}_3(\text{PPh}_3) + CO \quad (7)$$

$$2 + Ph_3P \xrightarrow{r_8} i\text{-PrC(O)Co(CO)}_3(\text{PPh}_3) + CO \quad (8)$$

The rate of CO evolution in reactions 7 and 8 at 5–25 °C was first order in 1 and 2 and was dependent of both Ph_3P and CO concentration in a complex way (Table IV and Figure 3).[11] Kinetic data in Table IV show that Ph_3P had a slightly positive and CO had a slightly negative effect on the rates of reactions 7 and 8.

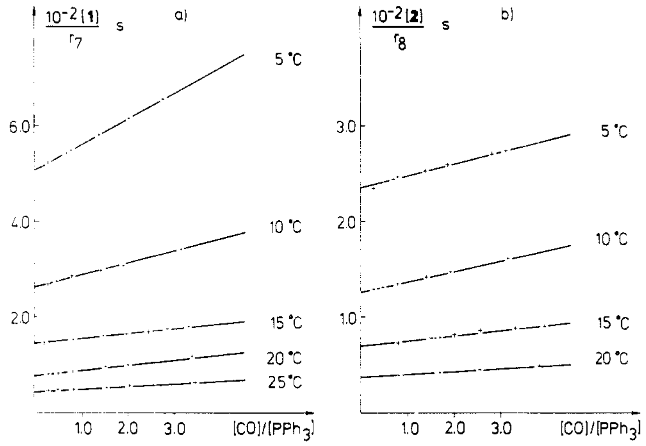
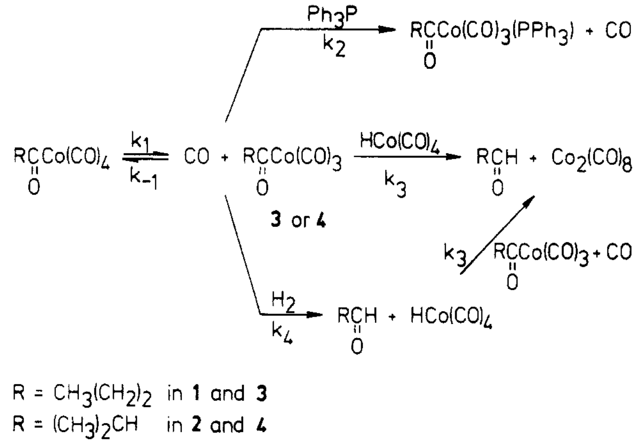


Figure 3. Kinetic data of reactions 7 and 8 in *n*-heptane at different temperatures plotted as [RC(O)Co(CO)$_4$]/*r* vs. [CO]/[Ph_3P]: a, R = *n*-C_3H_7; b, R = *i*-C_3H_7.

Scheme I



The observed negative effect of CO on the rates of reactions 3–8 can be rationalized by assuming the formation of an acylcobalt tricarbonyl in small concentrations followed by its reaction with either Ph_3P, HCo(CO)$_4$, or H_2 in competition with CO (Scheme I)

The kinetic measurements yielded linear plots of [acyl]/$r_{3,4}$ vs. [CO]/[HCo(CO)$_4$], [acyl]/$r_{5,6}'$ vs. [CO]/[H_2] (Figure 2), and [acyl]/$r_{7,8}$ vs. [CO]/[Ph_3P] (Figure 3) according to the expected rate laws for Scheme I using steady-state approximation for the acylcobalt tricarbonyl intermediate (eq 9–11). The rate constants k_{-1}/k_1k_2, k_{-1}/k_1k_3, k_{-1}/k_1k_4, and $1/k_1$ for Scheme I could be therefore

$$[\text{RC(O)Co(CO)}_4]/r_{7,8} = k_{-1}[\text{CO}]/k_1k_2[\text{Ph}_3\text{P}] + 1/k_1 \quad (9)$$

$$[\text{RC(O)Co(CO)}_4]/r_{3,4} = k_{-1}[\text{CO}]/k_1k_3[\text{HCo(CO)}_4] + 1/k_1 \quad (10)$$

$$[\text{RC(O)Co(CO)}_4]/r_{5,6}' = k_{-1}[\text{CO}]/k_1k_4[\text{H}_2] + 1/k_1 \quad (11)$$

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[11] Constant first-order rates, independent of phosphine concentration, have been found for the substitution of CO by Ph_3P for a great number of acylcobalt tetracarbonyls in diethyl ether solution. The rate constants of these reactions were regarded as a measure of the rate of CO dissociation from the acylcobalt tetracarbonyl.[12]

[12] Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 651.

Table I

a. Kinetic Data for Reactions of **1** and **2** with $HCo(CO)_4$ (Eq 3 and 4) at 25 °C in *n*-Heptane Solutions

10^2[**1**], M	10^2[**2**], M	10^2[**3**], M	10^2[CO],[a] M	$10^6 r_3$,[b] $M \cdot s^{-1}$	$10^6 r_4$,[b] $M \cdot s^{-1}$
0.74		1.22	1.08	1.91	
1.76		1.22	1.08	4.53	
3.10		1.22	1.08	7.95	
5.12		1.22	1.08	12.84	
1.22		1.07	1.08	2.75	
1.22		2.21	1.08	5.62	
1.22		3.46	1.08	8.70	
1.22		4.26	1.08	10.65	
1.22		5.48	1.08	13.47	
1.22		1.22	0.40	8.40	
1.22		1.22	0.47	7.04	
1.22		1.22	0.63	5.35	
1.22		1.22	1.07	3.14	
1.22		1.22	2.25	1.49	
	0.43	1.22	1.08		1.47
	1.34	1.22	1.08		5.06
	2.86	1.22	1.08		9.83
	3.72	1.22	1.08		12.59
	4.86	1.22	1.08		14.35
	5.89	1.22	1.08		20.08
	1.22	0.61	1.08		2.08
	1.22	1.64	1.08		5.53
	1.22	3.15	1.08		10.35
	1.22	4.56	1.08		15.05
	1.22	5.44	1.08		17.90
	1.22	6.75	1.08		21.40
	1.22	1.22	0.24		18.41
	1.22	1.22	0.28		15.43
	1.22	1.22	0.42		10.41
	1.22	1.22	0.53		8.37
	1.22	1.22	1.07		4.61
	1.22	1.22	2.00		2.56

b. Kinetic Data for Reactions of **1** and **2** with H_2 (Eq 5 and 6) at 25 °C in *n*-Heptane Solutions

10^2[**1**], M	10^2[**2**], M	10^3[H_2],[c] M	10^3[CO],[a] M	$10^7 r_5$,[b] $M \cdot s^{-1}$	$10^7 r_6$,[b] $M \cdot s^{-1}$
1.37		2.14	5.29	0.80	
1.18		2.60	4.10	1.08	
0.57		3.28	2.38	1.13	
1.35		3.28	2.38	2.68	
2.14		3.28	2.38	4.23	
1.21		3.70	1.30	4.93	
	1.29	2.15	5.32		1.30
	1.19	2.61	4.12		1.88
	2.41	2.15	5.32		2.43
	2.35	2.61	4.12		3.71
	3.84	2.15	5.32		3.87
	1.31	3.25	2.36		4.50
	3.50	2.59	4.12		5.53
	4.05	2.59	4.08		6.40
	4.96	3.25	4.08		7.83
	1.27	1.29	0.45		8.99
	1.27	3.76	1.29		9.00

[a] Calculated from p_{CO} and the solubility of CO in *n*-heptane.[10] [b] Initial rates measured by IR. [c] Calculated from p_{H_2} and the solubility of H_2 in *n*-heptane.[9]

Table II. Kinetic Isotope Effects on the Initial Rates of the Reactions 3–6 at 25 °C in *n*-Heptane Solutions

10^2[**1**], M	10^2[**2**], M	10^2[$HCo(CO)_4$], M	10^3[H_2],[a] M	10^3[CO],[b] M	$10^7 r_3$, $M \cdot s^{-1}$	$10^7 r_4$, $M \cdot s^{-1}$	$10^7 r_5$, $M \cdot s^{-1}$	$10^7 r_6$, $M \cdot s^{-1}$
1.21		1.07		10.8	27.2			
1.00		0.68[c]		10.7	17.9			
	1.34	1.11		10.7		46.0		
	0.98	1.14[c]		10.7		50.1		
1.21			3.70	1.30			4.9	
1.89			3.92[d]	1.07			10.4	
	1.27		3.76	1.29				9.0
	1.44		3.92[d]	1.07				14.4

[a] Calculated from p_{H_2} (or p_{D_2}) and the solubility of H_2 (or D_2) in *n*-heptane.[9] [b] Calculated from p_{CO} and the solubility of CO in *n*-heptane.[10] [c] $DCo(CO)_4$. [d] D_2.

derived from the kinetic data as the slopes and the intercepts of Figures 2 and 3 and are collected in Tables V and VI. It should be noted here, that the numbers compiled in Tables V and VI were calculated by regression analysis of the measured values and not evaluated from Figures 2 and 3.

The acyl complexes **1** and **2** are stable in hydrocarbon solution at room temperature under an atmospheric

Table III. Effect of CO and H_2 on the Conversion of 1 or 2 into $HCo(CO)_4$, $Co_2(CO)_8$, and the Corresponding *n*-Butyraldehyde or Isobutyraldehyde under Pressure at 45 °C (Initial Concentrations [1] = [2] = 0.015 M)

p_{CO}, bar	p_{H_2}, bar	time, min	convn of 1, %	convn of 2, %	$[HCo(CO)_4]/[Co_2(CO)_8]$
1	80	10			0.00[a]
1	80	10	68		0.94
1	80	10		>95	0.62
10	50	10		38	
10	50	15		63	1.63
10	50	20		76	
10	50	35		87	
14	50	25	39		1.92
20	50	15		36	
20	50	25	25		1.78
60	50	15		12	
60	50	30		25	0.77
66	50	25	8		
120	50	15		6	
100	50	30		14	
120	50	25	4		

[a] Experiment started with $[Co_2(CO)_8]$ = 0.015 M, without 1 or 2.

Table IV. Initial Rates of CO Substitution in 1 and 2 by Ph_3P at Various Conditions in *n*-Heptane Solution

temp, °C	$10^3[1]$, M	$10^3[2]$, M	$10^2[Ph_3P]$, M	$10^3[CO]$,[a] M	$10^6 r_7$, $M \cdot s^{-1}$	$10^6 r_8$, $M \cdot s^{-1}$
5	4.53		3.33	9.17	8.7	
5	4.53		1.20	9.18	8.3	
5	4.53		0.67	9.18	7.8	
5	4.53		0.45	9.18	7.4	
5	4.53		0.67	4.54	8.4	
5	4.53		0.67	18.4	6.9	
5		4.53	3.33	9.17		19.4
5		4.53	1.20	9.27		18.4
5		4.53	0.67	9.27		18.0
5		4.53	0.50	9.27		17.6
5		4.53	0.30	9.27		16.6
5		4.53	0.67	4.66		18.6
5		4.53	0.67	18.7		16.8
15	4.53		0.30	9.89	14.3	
15	2.47		0.35	9.93	25.5	
15	4.53		0.40	9.75	27.0	
15	4.53		0.50	9.85	27.8	
15	0.90		0.67	9.85	5.6	
15	1.81		0.67	9.86	11.5	
15	4.53		0.67	9.89	28.3	
15	9.04		0.67	9.86	57.6	
15	4.53		1.20	9.88	29.8	
15	4.52		5.00	9.88	31.2	
15		2.46	0.25	9.92		27.3
15		5.00	0.30	9.94		56.8
15		2.46	0.39	9.92		29.6
15		5.00	0.50	9.94		58.7
15		1.00	0.67	9.93		12.4
15		5.00	0.67	9.82		25.8
15		10.0	0.67	9.84		129
15		2.46	0.59	9.92		31.5
15		2.00	0.67	9.82		25.8
15		2.46	1.25	9.92		33.7

[a] Calculated from p_{CO} and the solubility of CO in *n*-heptane.[10].

pressure of CO. Decomposition leading to $Co_2(CO)_8$, CO, propene, traces of propane, and the corresponding butyraldehydes[13] occurs only above 50 °C[15] at a rate convenient to measure by IR and gas evolution (Table VII). Under 80 bar CO no change of the acyl concentration or structure could be detected by IR in 1 h at 80 °C. In hydrocarbon solutions we never observed the isomerization of unreacted acyls during any of our experiments.[16]

Discussion

The Mechanism of Cleavage. The inhibiting effect of CO on the reactions of 1 and 2 with $HCo(CO)_4$, H_2, or Ph_3P suggests a tricarbonyl complex as intermediate formed by CO dissociation from the corresponding acylcobalt tetracarbonyl. This intermediate may react either with CO reforming the tetracarbonyl complex or with other reagents such as Ph_3P, $HCo(CO)_4$, and H_2 leading to the

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(13) Slow disproportionation of the products from the reaction of butyryl halides and $NaCo(CO)_4$ in ether at room temperature into propene and a mixture of *n*-butyraldehyde and isobutyraldehyde have been reported.[14]

(14) Rupilius, W.; Orchin, M. *J. Org. Chem.* **1972**, *37*, 936.

(15) Pyrolysis of in situ formed propionylcobalt tetracarbonyl at 170 °C yielding 50% ethene, propionaldehyde, and a little ethane has been reported.[6b]

(16) Extensive isomerization of 1 and 2 during their formation from the corresponding acyl halide and $KCo(CO)_4$ at 25 °C in ether has been reported.[17] The conclusion was based on the formation of isomeric carboxylic acid *n*-propyl esters after decomposing the acyl complexes with I_2 + *n*-propyl alcohol.

(17) (a) Takegami, Y.; Yokokawa, C.; Watanabe, Y.; Okuda, Y. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 181. (b) Takegami, Y.; Yokokawa, C.; Watanabe, Y.; Masada, H.; Okuda, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 787.

Table V. Rate Constants[a] for Reactions 3-8 at Various Temperatures

temp, °C	compd	k_{-1}/k_1k_2, s	$1/k_1$, s	k_{-1}/k_1k_3, s	$1/k_1$, s	k_{-1}/k_1k_4, s	$1/k_1$, s
5	1	54 ± 1	506 ± 2				
10	1	25 ± 2	261 ± 3				
15	1	10 ± 1	143 ± 2				
20	1	11 ± 0.2	77 ± 0.3	7673 ± 8	82 ± 5		
25	1	5 ± 0.3	43 ± 0.5	4332 ± 16	51 ± 2	139 186 ± 48	68 ± 32
25	1			4637[b]		133 044[c]	
30	1			2464 ± 9	31 ± 8	73 316 ± 36	29 ± 26
35	1			1440 ± 11	19 ± 9	36 396 ± 12	20 ± 8
40	1			875 ± 9	12 ± 6	17 420 ± 8	10 ± 5
45	1					8712 ± 2	6 ± 1
5	2	13 ± 2	233 ± 4				
10	2	11 ± 0.4	126 ± 1				
15	2	5 ± 1	69 ± 3				
20	2	3 ± 0.5	37 ± 1	5625 ± 5	47 ± 5		
25	2			3297 ± 4	27 ± 4	80 286 ± 2	28 ± 1
25	2			2018[b]		71 920[c]	
30	2			1913 ± 6	17 ± 6	42 416 ± 8	18 ± 6
35	2			1208 ± 3	10 ± 4	18 852 ± 2	11 ± 2
40	2					10 848 ± 8	7 ± 3
45	2					5382 ± 2	5 ± 1

[a] Deviations represent 95% confidence level. [b] From experiments using $DCo(CO)_4$. [c] From experiments using D_2.

Table VI. Temperature Dependence of the Rate Constants and the Calculated Thermodynamic Parameters[a]

compd	temp range, °C		$\Delta H^{\ddagger}_{25\,°C}$, kcal·mol^{-1}	$\Delta S^{\ddagger}_{25\,°C}$, eu
1	5–45	$\log k_1 = (13.22 \pm 0.08) - (4427 \pm 23)/T$	19.6 ± 0.1	0.1 ± 0.4
2	5–45	$\log k_1 = (13.20 \pm 0.21) - (4330 \pm 60)/T$	19.2 ± 0.3	0.0 ± 1
1	5–25	$\log k_1k_2/k_{-1} = (12.37 \pm 2.11) - (3901 \pm 608)/T$	17.2 ± 2.8	−3.8 ± 9.7
2	5–20	$\log k_1k_2/k_{-1} = (12.02 \pm 2.24) - (3669 \pm 640)/T$	16.2 ± 2.9	−5.4 ± 10.3
1	20–40	$\log k_1k_3/k_{-1} = (10.92 \pm 0.25) - (4337 \pm 78)/T$	19.2 ± 0.4	−10.5 ± 1.2
2	20–35	$\log k_1k_3/k_{-1} = (6.94 \pm 3.79) - (3121 \pm 356)/T$	13.7 ± 1.6	−53.8 ± 42
1	25–45	$\log k_1k_4/k_{-1} = (14.10 \pm 1.34) - (5740 \pm 417)/T$	25.7 ± 1.9	4.1 ± 6.2
2	25–45	$\log k_1k_4/k_{-1} = (13.78 \pm 1.56) - (5570 \pm 480)/T$	26.4 ± 2.2	2.7 ± 11.2

[a] Deviations represent 95% confidence level; k_1 (s^{-1}); k_1k_2/k_{-1} (s^{-1}); k_1k_3/k_{-1} (s^{-1}); k_1k_4/k_{-1} (s^{-1}); T = temperature in Kelvin.

Table VII. Initial Rate of Decomposition (r) of 1 and 2 under CO at 750 mmHg Total Pressure in n-Octane Solution ([1] = 0.0137 M; [2] = 0.0147 M)

	10^6r, M·s^{-1}	
temp, °C	1	2
60	0.82	1.1
70	5.3	7.3
80	31	48
80	0.0[a]	0.0[a]

[a] Under 80 bar CO.

products according to Scheme I. The reasonable agreement of the rate constant k_1 in these reactions (Table V) derived from the kinetic measurements assuming steady-state concentrations for **3** or **4** supports this assumption. The equilibria leading to **3** and **4** are certainly far on the side of the tetracarbonyls because the IR spectra of **1** or **2** did not show the presence of tricarbonyls in detectable concentrations in the absence of Ph_3P, $HCo(CO)_4$, H_2, and CO even at 45 °C.

The formation of propene and butyraldehydes as main products by thermal decomposition of **1** or **2** above 50 °C does also not support in the case of **1** and **2** the suggestion[18] and the results published for n-hexanoylcobalt tetracarbonyl[7] according to which aldehyde formation should be preceded by homolytic dissociation of the Co–acyl bond. The acyl radicals would in the absence of an appropriate reagent decarbonylate to the corresponding alkyl radicals which in turn would lead to a 1:1 mixture of alkene and alkane by disproportionation together with radical combination products. At 80 °C the decomposition of **1** and **2**, however, yielded nearly 50% aldehyde, 49% propene, and only 1% propane. This is in accord with the results of the high-temperature (170 °C) decomposition of propionylcobalt tetracarbonyl[6b] and the disproportionation of acylcobalt tetracarbonyls under N_2 at room temperature.[14] Apparently the spontaneous thermal reaction of acylcobalt tetracarbonyls is the reverse of their formation from alkenes, $HCo(CO)_4$, and CO (eq 12) and the formation of aldehyde and $Co_2(CO)_8$ during this decomposition is due to the secondary reaction between the acyl complexes and $HCo(CO)_4$ (eq 13).

$$RCH_2CH_2C(O)Co(CO)_4 \xrightarrow{\Delta} RCH{=}CH_2 + HCo(CO)_4 + CO \quad (12)$$

$$RCH_2CH_2C(O)Co(CO)_4 + HCo(CO)_4 \rightarrow RCH_2CH_2CHO + Co_2(CO)_8 \quad (13)$$

The inhibiting effect of CO on the reaction of **1** or **2** with H_2 could be observed up till 120 bar (Table III), suggesting that the mechanism of cleavage does not change even under the conditions of high-pressure catalytic hydroformylation. As to our opinion a radical mechanism of aldehyde formation may be therefore ruled out as an alternative for the hydroformylation of aliphatic olefins with unsubstituted cobalt carbonyls as catalysts.

Such a mechanism remains a distinctive possibility, however, for the Shell process which uses phosphine-substituted cobalt carbonyls as catalysts.[19] It has been shown that phosphine substitution favors the radical pathway in the case of acylmanganese carbonyl complexes because of disfavoring CO loss and enhancing steric destabilization.[20] A similar effect may be reasonably expected for analogous cobalt complexes.

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Table VIII. Comparison of Rate Constants for 25 °C

	1	2
k_1, s^{-1}	0.0233	0.0468
k_1k_2/k_{-1}, s^{-1}	0.19	0.51
$10^5k_1k_3/k_{-1}$, s^{-1}	23.3 27.4[a]	29.5 49.5[a]
$10^5k_1k_4/k_{-1}$, s^{-1}	0.69 0.75[b]	1.21 1.39[b]
k_2/k_{-1}	8.2	11
k_3/k_{-1}	0.010	0.0063
k_4/k_{-1}	0.00030	0.00026
k_3/k_3[a]	0.85	0.60
k_4/k_4[b]	0.92	0.87
k_3/k_4	34	24

[a] With $DCo(CO)_4$. [b] With D_2.

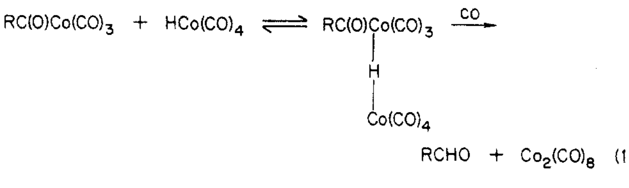
Dihydrogen vs. $HCo(CO)_4$ as a Reductant. As can be seen from the k_3/k_4 values in Table VIII, $HCo(CO)_4$ is at 25 °C 34 or 24 times more reactive than H_2 against 1 or 2, respectively. The higher reactivity of $HCo(CO)_4$ seems to be general for alkyl- or acylcobalt carbonyls under such conditions: the same ratio was found to be 12 in the case of $EtOC(O)Co(CO)_4$[4] and 130 with $EtOC(O)CH_2Co(CO)_4$.[5]

In drawing conclusions from these data with regard to the relative role of H_2 or $HCo(CO)_4$ under conditions of catalytic hydroformylation two important differences have to be considered. First, under the high pressures used in the catalytic process the concentration of H_2 in the reaction mixture will be about 2 orders of magnitude higher than that of $HCo(CO)_4$.[3] Second, due to the significantly larger enthalpies of activation for the reactions with H_2 (see Table VI), at the temperatures necessary for the catalytic process (>100 °C) the relative reactivity of H_2 will be much nearer to that of $HCo(CO)_4$ or even surpass it. Thus, for example, extrapolating the k_3/k_4 values to 80 °C, we obtain 6.2 for complex 1 and 1.2 for complex 2.

It can be stated therefore that mainly H_2 will be responsible for aldehyde formation from acylcobalt carbonyls under the industrial conditions of hydroformylation and the reaction with $HCo(CO)_4$ will only play a minor role. This conclusion is in agreement with the most recent measurements performed under catalytic conditions[3] and confirms the original proposal of Heck[6] put forward 25 years ago.

The inverse isotope effects obtained with D_2 and $DCo(CO)_4$ (Table VIII) are presumably of thermodynamic origin. We suggest that in both cases adducts are formed as primary products from the acylcobalt tricarbonyls 3 or 4 and the reductants in equilibrium reactions and that these adducts are more stable with the deuterium-containing species than with the hydrogen-containing analogues. Accordingly we propose the fine mechanisms (14) and (15) for steps 3 and 4 of Scheme I. Reversible addition of H_2 or D_2 to coordinatively unsaturated transition-metal complexes is well documented;[21a] H- (or D-) bridged structures are also well-known[21b] and have been already invoked also as intermediates in similar reactions.[22]

$$RC(O)Co(CO)_3 + H_2 \rightleftharpoons RC(O)CoH_2(CO)_3 \xrightarrow{CO} RCHO + HCo(CO)_4 \quad (14)$$



$$RC(O)Co(CO)_3 + HCo(CO)_4 \rightleftharpoons RC(O)Co(CO)_3{-}H{-}Co(CO)_4 \xrightarrow{CO} RCHO + Co_2(CO)_8$$

(15)

Experimental Section

General Techniques. Infrared spectra were recorded on a Carl Zeiss Jena IR 75 spectrophotometer using a thermostated KBr cuvette. Analysis of the volatile compounds was performed on an analytical Hewlett-Packard Model 5830A gas chromatograph or on a Chromatron GCHF 18.3-1 gas chromatograph. All manipulations involving air-sensitive organometallic compounds were carried out by using anaerobic techniques.[23]

Materials. Hydrocarbon solvents were dried on sodium wire and were distilled under a CO atmosphere. Stock solutions of $HCo(CO)_4$ (0.6 M) were prepared in *n*-heptane from $Co_2(CO)_8$, DMF, and concentrated HCl.[24] $DCo(CO)_4$ was prepared from $HCo(CO)_4$ solutions by hydrogen and deuterium exchange with a 50-fold molar excess of D_2O.[25] Isotopic purity was >95% as calculated from mass spectrometric measurements of its decomposition products. The concentration of $HCo(CO)_4$ and $DCo(CO)_4$ solutions were determined by 0.1 N alkaline titration at 0 °C under CO. *n*-Butyrylcobalt tetracarbonyl (1) and isobutyrylcobalt tetracarbonyl (2) were prepared by the published method[8] from $HCo(CO)_4$ and ethylketene or dimethylketene, respectively. Stock solutions of the acylcobalt tetracarbonyls (0.2 M) in *n*-heptane were used in the kinetic experiments.

Kinetic runs using $HCo(CO)_4$ were performed under CO in a thermostated (±0.05 °C) reaction vessel connected to a 5-L buffer flask in order to maintain the pressure constant (0.2–3 bar). The actual total pressure was determined in millimeters of Hg by using an open mercury manometer measuring the pressure difference between the atmosphere and the reaction vessel. The reaction was started by injecting 0.6 M solutions of $HCo(CO)_4$ in *n*-heptane into vigorously stirred solutions of the acyl complexes in *n*-heptane. The change of IR spectra was followed from samples withdrawn by a gas-tight syringe and filled through a three-way Hamilton valve and Teflon tubing into the 0.11- or 0.25-mm KBr cuvette. [Absorbancies (*n*-heptane): 2116 ($\epsilon_M(HCo(CO)_4)$ 330 ± 10),[26] 2105 (ϵ_M(**1**) 1420),[27] 2104 (ϵ_M(**2**) 1490),[27] 1857 ($\epsilon_M(Co_2(CO)_8)$ 1735),[28] 1735 ($\epsilon_M(CH_3CH_2CH_2CHO)$ 208), 1742 ($\epsilon_M((CH_3)_2CHCHO)$ 228), 1717 (ϵ_M(**1**) 418),[27] 1737 (ϵ_M(**2**) 500),[27] 1699 cm^{-1} (ϵ_M(**2**) 370 cm^2 $mmol^{-1}$).[27]]

Reduction of 1 and 2 with H_2. In the kinetic runs H_2 + CO mixtures were used and the reactions were started by injecting 0.2 M solutions of the acyl complex in *n*-heptane into vigorously stirred *n*-heptane under a constant pressure between 0.2 and 3 bar. The composition of the gas mixture was checked by gas chromatography (3 m, Porapack Q, 25 °C, 5 mL/min of Ar, TCD). The change of IR spectra was followed as described above.

Reduction of 1 and 2 with H_2 under 80-Bar Pressure. The 5-mL samples of 0.015 M solutions of 1 or 2 in *n*-heptane were placed at room temperature under CO in a 20-mL stainless-steel rocking autoclave and pressurized to 80 bar with H_2. After 10-min agitation at 45 °C the autoclave was cooled to +5 °C and IR spectra were taken immediately after the pressure was released by using a cold (+5 °C) CaF_2 IR cell. The spectrum showed 68% conversion of 1 into *n*-butyraldehyde and $HCo(CO)_4$ + $Co_2(CO)_8$ in a 1:1.06 molar ratio. In the case of 2, 95% conversion into isobutyraldehyde and a 1:1.93 ratio of $HCo(CO)_4$ to $Co_2(CO)_8$ was found. In blank experiments using a 0.015 M solution of $Co_2(CO)_8$ in *n*-heptane no detectable amount of $HCo(CO)_4$ could be found by IR analysis, after 10-min agitation at 45 °C under 80 bar H_2. The same technique was used in experiments performed under p_{H_2} = 50 bar and p_{CO} = 10–120 bar pressures.

Decomposition of 1 and 2 under atmospheric pressure of CO was followed by using the gasometric apparatus and IR technique

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described before. The rate of gas evolution corresponded to the rate of acyl decomposition between 50 and 80 °C. During the decomposition of 1 or 2, isomerization of the acyl compounds did not occur. The composition of the reaction mixture was checked by IR with the ν(CO) bands of terminal CO ligands as a control of concentration and the acyl ν(CO) bands as a control of structure.

The organic products of decomposition were investigated in experiments performed at 80 °C and 1-h reaction time in sealed 20-mL ampules with 2-mL samples of 0.02 M solutions of 1 and 2 in *n*-octane containing *n*-pentane as internal reference for quantitative GC analysis (3 m, *n*-octane/Porasil C, 50 °C, 15 mL/min of Ar, FID). The decompositions yielded 45–48% propene, 1% propane, and 37% *n*-butyraldehyde (if starting from 1) or 45% isobutyraldehyde (if starting from 2).

Stability of 1 and 2 at 80 °C under CO Pressure. The 5-mL samples of 0.014 M solutions of 1 or 2 in *n*-heptane were placed at room temperature under CO in a 20-mL stainless-steel rocking autoclave and pressurized to 80 bar with CO. After 1-h agitation at 80 °C, the IR spectra of the reaction mixtures at room temperature showed within 1% accuracy unchanged concentrations of the acyl complexes as measured at 2105 cm^{-1}. No traces of isomerized acylcobalt tetracarbonyl could be recognized in the characteristic organic ν(CO) range of 1 and 2.

Reaction of Ph_3P with 1 and 2 was performed in the gasometric apparatus described above and started by injecting the acyl stock solutions into solutions containing known amounts of Ph_3P. In all kinetic experiments initial rates were calculated from graphical plots below 15% conversion.

Registry No. 1, 38722-67-7; 2, 38784-32-6; $HCo(CO)_4$, 16842-03-8; Hz, 1333-74-0; CO, 630-08-0; *n*-PrCHO, 123-72-8; *i*-PrCHO, 78-84-2; $Co2(CO)_8$, 10210-68-1; *n*-PrC(O)Co$(CO)_3(PPh_3)$, 34151-25-2; *i*-PrC(O)Co$(CO)_3(PPh_3)$, 99495-72-4; PPh_3, 603-35-0; propene, 115-07-1.

Rhodium(III)-to-Rhodium(I) Alkyl Transfer: A Rhodium Macrocycle Which Is Both Nucleophile and Leaving Group

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Received February 12, 1985

The rhodium(I) macrocycles $Rh^I(BPDOBF_2)$ (**1a**) and $Rh^I(PPDOBF_2)$ (**1b**) are strong nucleophiles toward alkyl halides and may also be alkylated by their rhodium(III) alkyl halide adducts $R'-Rh^{III}(BPDOBF_2)-X$ and $R'-Rh^{III}(PPDOBF_2)-X$ (**2a and 2b**), respectively. In the latter process, **1a,b** act as both nucleophile and leaving group. We have studied the kinetics of alkyl exchange between, e.g., **1a** and **2b** by ^1H NMR and the rate constants are $(5.8 \pm 0.5) \times 10^{-3}\ M^{-1}\ s^{-1}$ for methyl exchange (R′ = Me, X = I) and $(6.4 \pm 1.0) \times 10^{-2}\ M^{-1}\ s^{-1}$ for benzyl exchange ($R' = PhCH_2$, X = Cl). Other alkyl groups do not participate in this reaction. These data are consistent with rhodium(I) attack at carbon; the process may be viewed as a carbon-bridged two-electron transfer. Halide-bridged electron transfer is implied in the much faster exchange ($k > 0.5\ M^{-1}\ s^{-1}$) between **1a,b** and their rhodium(III) dichloride derivatives **3a** and **3b**.

Introduction

Low-valent transition-metal complexes exhibit nucleophilic behavior in many of their oxidative-addition reactions with alkyl halides, leading to the formation of metal–carbon bonds via an S_N2-like process.[1] The ability of metal centers to function as leaving groups is less widely recognized, despite scattered reports.[2] These include several examples of essentially degenerate nucleophilic reactions in which the same type of metal center serves as both nucleophile and leaving group[2a,b,c,e] (eq 1). The

$$M_1^n + R'-M_2^{n+2} \rightleftharpoons R'-M_1^{n+2} + M_2^n \qquad (1)$$

latter reactions result in the transfer of an alkyl group from one metal center to another and may be viewed as carbon-bridged inner-sphere two-electron-transfer processes.[3] When the two centers are distinguished by a minor ligand modification, these exchange reactions are nearly thermoneutral, and their study should throw light on the kinetic factors which control two-electron processes that make and break metal–carbon bonds.[4]

We encountered a novel example of the process represented by eq 1 in the course of our studies on the oxidative addition of alkyl halides to a Rh(I) macrocycle.[1,5] We

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[4] Several groups have undertaken the analysis of "intrinsic" kinetic barriers to nucleophilic reactions in which the Marcus theory[4a] of electron transfer is applied to reactivity data for methyl transfer in the gas phase[4b–d] or in solution.[4e] Endicott's group has made an extensive analysis of the analogous S_H2 mechanism implicated in methyl and halide transfer between Co(II) and Co(III) macrocycles.[4f–h] (See also ref 4i.) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155–196. (b) Shaik, S. S.; Pross, A. *J. Am. Chem. Soc.* **1982**, *104*, 2708–2719. (c) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7694–7696. (d) Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 2672–2680. Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993–5999. (e) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87–157. (f) Endicott, J. F.; Wong, C.-L.; Ciskowski, J. M.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1980**, *102*, 2100–2103. (g) Endicott, J. F.; Balakrishnan, K. P.; Wong, C.-L. *J. Am. Chem. Soc.* **1980**, *102*, 5519–5526. (h) Durham, B.; Endicott, J. F.; Wong, C.-L.; Rillema, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 847–857. (i) Johnson, M. D. *Acc. Chem. Res.* **1983**, *16*, 343–349.

[5] Preliminary report: Collman, J. P.; MacLaury, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 3019–3020. We have since adopted a modified nomenclature for the macrocyclic ligands: $(PPDOBF_2)$ = [difluoro[*N,N*′-bis(3-pentanon-2-ylidene)-1,3-diaminopropane)dioximato]borate], and $(BPDOBF_2)$ = [difluoro[*N,N*′-bis(3-butanon-2-ylidene)-1,3-diaminopropane)dioximato]borate]. Other abbreviations: PPN^+ = bis(triphenylphosphoranediyl)nitrogen(1+) ion.

0276-7333/86/2305-0215$01.50/0