Kinetics and Mechanism of the Reaction of HCo(CO)₄ with Ethyl Acrylate. Conversion of (1-(Ethoxycarbonyl)ethyl)cobalt Tetracarbonyl to (3-(Ethoxycarbonyl)propionyl)cobalt Tetracarbonyl

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Received January 17, 1986

The dicobalt octacarbonyl catalyzed reaction of hydridocobalt tetracarbonyl and ethyl acrylate in the presence of carbon monoxide results under kinetically controlled conditions (<10 °C) in the formation of ethyl propionate, ethyl 2-formylpropionate, and (1-(ethoxycarbonyl)ethyl)cobalt tetracarbonyl. Under thermodynamic control (>25 °C) the latter complex is transformed into (3-(ethoxycarbonyl)propionyl)cobalt tetracarbonyl which is the precursor of ethyl 3-formylpropionate. This temperature effect is in accordance with the known influence of temperature on the distribution of isomeric aldehydes in the catalytic hydroformylation of ethyl acrylate.
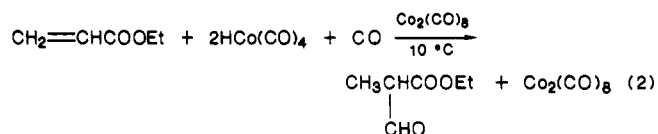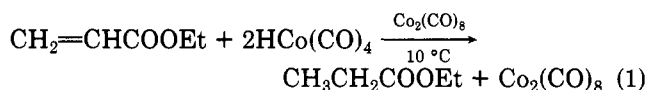
Introduction

It is known that temperature has a strong effect on the isomeric composition of aldehydes in the cobalt-catalyzed hydroformylation of styrene[1] and ethyl acrylate.[2] In both cases rising the temperature favors the formation of the straight chain isomer.

The reaction between HCo(CO)₄ and olefin is regarded as a component of the hydroformylation catalytic cycle in the presence of cobalt carbonyls.[3] The main products of this stoichiometric reaction are aldehydes (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. Saturated hydrocarbons are formed as byproducts. In the case of styrene we have shown recently that both (2-phenyl propionyl)cobalt tetracarbonyl and ethylbenzene are formed through a radical pair mechanism.[4] The branched chain acyl is the kinetically controlled product which can isomerize to the thermodynamically more stable (3-phenylpropionyl)cobalt tetracarbonyl. This explains the effect of temperature on the ratio of aldehyde isomers in the catalytic reaction of styrene. A similar explanation may be anticipated in the case of ethyl acrylate too. We now wish to report on the reaction between HCo(CO)₄ and ethyl acrylate which shows a completely different kinetic behavior resembling that observed with aliphatic olefins.[5]

Results

In the presence of Co₂(CO)₈ ethyl acrylate reacts readily with HCo(CO)₄ forming ethyl propionate as hydrogenated product and ethyl 2-formylpropionate as hydroformylated product (eq 1 and 2). In the absence of Co₂(CO)₈ the

$$CH_2{=}CHCOOEt + 2HCo(CO)_4 \xrightarrow[10\ °C]{Co_2(CO)_8}$$
$$CH_3CH_2COOEt + Co_2(CO)_8 \quad (1)$$

$$CH_2{=}CHCOOEt + 2HCo(CO)_4 + CO \xrightarrow[10\ °C]{Co_2(CO)_8}$$
$$\underset{\underset{CHO}{|}}{CH_3CHCOOEt} + Co_2(CO)_8 \quad (2)$$

hydrogenation and the hydroformylation showed an induction period. The rate of ethyl propionate formation and the rate of carbon monoxide uptake is 0.5 order in Co₂(CO)₈ (Table I) and first order in ethyl acrylate and is rather complex with respect to HCo(CO)₄ and CO concentration (Table II). The data in Table II show that HCo(CO)₄ has a stronger influence on the rate of ethyl propionate formation than on the rate of CO uptake. Similarly the retarding effect of CO is more pronounced in reaction 1 than in reaction 2. The ratio of the rates of CO uptake (r_{CO}) and ethyl propionate formation (r_H) is a function of the ratio of CO and HCo(CO)₄ concentrations as can be seen in Figure 1.

In a typical experiment at 10 °C with the initial concentrations of $[HCo(CO)_4]_0 = 0.030$ M, $[Co_2(CO)_8]_0 = 0.098$ M, and $[CH_2{=}CHCOOEt]_0 = 0.200$ M under 1 bar of CO, the CO uptake practically stopped after 30 min at 0.25 mol/(mol of HCo(CO)₄). At that time all HCo(CO)₄ was consumed. On the basis of GC analyses 10% of HCo(CO)₄ was consumed in reaction 1 and 50% in reaction 2. The missing 40% of HCo(CO)₄ was found in the reaction mixture in the form of (1-(ethoxycarbonyl)ethyl)cobalt tetracarbonyl formed according to reaction 3.

$$CH_2{=}CHCOOEt + HCo(CO)_4 \xrightarrow[10\ °C]{Co_2(CO)_8} \underset{\underset{Co(CO)_4}{|}}{CH_3CHCOOEt} \quad (3)$$
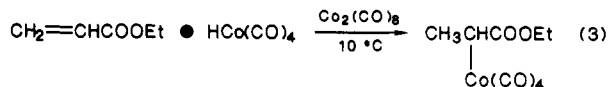
The infrared spectrum of the reaction mixture just after CO uptake has stopped (and Co₂(CO)₈ has been frozen out at -79 °C) showed ν(CO) bands typical for an alkylcobalt tetracarbonyl[6] at 2107 (m), 2041 (s), 2031 (vs), and 2021 (vs) cm⁻¹ and a band characteristic for a carboxylic ester group at 1716 (w) cm⁻¹ (Figure 2a).[7] When PPh₃ was

(1) (a) Botteghi, C.; Consiglio, G.; Pino, P. *Chimia* 1972, 26, 141. (b) Botteghi, C.; Branco, M.; Marchetti, M.; Saba, A. *J. Organomet. Chem.* 1978, 161, 197. (c) Lai, R.; Ucciani, E. *J. Mol. Catal.* 1978, 4, 401.

(2) Falbe, J.; Huppes, N.; Korte, F. *Chem. Ber.* 1964, 97, 863.

(3) Pino, P.; Piacenti, F.; Bianchi, M. *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, pp 43–135.

(4) (a) Ungváry, F.; Markó, L. *Organometallics* 1982, 1, 1120. (b) Ungváry, F.; Markó, L. *J. Organomet. Chem.* 1983, 249, 411. (c) Bockman, T. M.; Garst, J. F.; King, R. B.; Markó, L.; Ungváry, F. *J. Organomet. Chem.* 1985, 279, 165.

(5) (a) Ungváry, F.; Markó, L. *J. Organomet. Chem.* 1981, 219, 397. (b) Ungváry, F. *Acta Chim. Acad. Sci. Hung.* 1982, 111, 117. (c) Ungváry, F.; Markó, L.; Bockman, T. M.; Garst, J. F.; King, R. B. *Isr. J. Chem.*, submitted for publication.

(6) Galamb, V.; Pályi, G. *Coord. Chem. Rev.* 1984, 59, 203.

(7) The same absorptions have been found recently for the product in the reaction of ethyl 2-bromopropionate with Na[Co(CO)₄] in diethyl ether at 0 °C.[8]

Table I. Effect of $Co_2(CO)_8$ Concentration in the Reaction of Ethyl Acrylate and $HCo(CO)_4$ on the Initial Rates of Carbon Monoxide Uptake (r_{CO}) and Ethyl Propionate Formation (r_H) at 10 °C in n-Octane Solution[a]

$[Co_2(CO)_8]_0$, M	$10^6 r_{CO}$, M·s^{-1}	$10^5 r_{CO}/[Co_2(CO)_8]_0$	$10^6 r_H$, M·s^{-1}	$10^5 r_H/[Co_2(CO)_8]_0$
0.0168	6.53	5.04	4.8	3.70
0.0189	6.83	4.97		
0.0565	12.0	5.07		
0.0960	15.5	5.00	11	3.55

[a] [CO] = 0.0102 M, $[HCo(CO)_4]_0$ = 0.0208 M, $[CH_2=CHCOOEt]_0$ = 0.200 M.

Table II. Effect of $HCo(CO)_4$ and CO Concentration in the Reaction of Ethyl Acrylate and $HCo(CO)_4$ on the Initial Rates of Carbon Monoxide Uptake (r_{CO}) and Ethyl Propionate Formation (r_H) at 10 °C in n-Octane Solution ($[CH_2=CHCOOEt]_0$ = 0.139 M)

$[HCo(CO)_4]_0$, M	$[Co_2(CO)_8]_0$, M	$10^2[CO]$ M	$10^6 r_{CO}$, M·s^{-1}	$10^6 r_H$, M·s^{-1}
0.0104	0.0168	1.036	3.0	1.2
0.0140	0.0168	1.020	3.62	
0.0208	0.0168	0.424	5.1	7.0
0.0208	0.0168	1.016	4.52	
0.0208	0.0168	1.036	4.34	2.5
0.0208	0.0168	2.812	4.0	0.7
0.0290	0.0168	1.020	5.4	
0.0297	0.0984	1.040	18.2[a,b]	
0.0297[c]	0.0984	1.040	18.4[a]	
0.0417	0.0178	1.036	6.10	7.1
0.0436	0.0172	1.036	13.2[d]	13[d]
0.0632	0.0168	1.023	7.2	
0.0904	0.0178	1.036	8.62	16

[a] $[CH_2=CHCOOEt]_0$ = 0.195 M. [b] In 30 min all $HCo(CO)_4$ was converted and the CO uptake practically stopped at 0.25 mol/mol of $HCo(CO)_4$. [c] $DCo(CO)_4$. [d] $[CH_2=CHCOOEt]_0$ = 0.269 M.
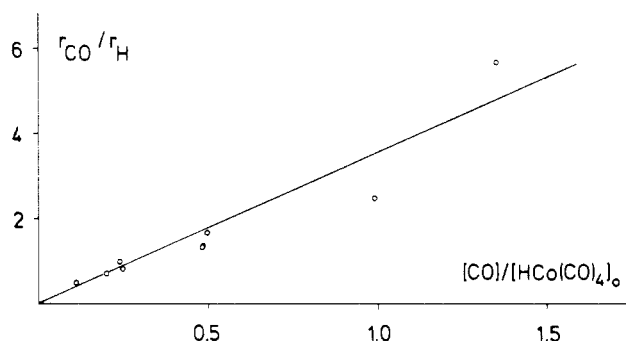
Figure 1. The ratio of experimental initial rates of CO uptake (r_{CO}) and ethyl propionate formation (r_H) vs. $[CO]/[HCo(CO)_4]_0$ at 10 °C.

added to this solution below 10 °C, a yellow crystalline triphenylphosphine derivative was formed without CO evolution. The ^1H NMR spectrum of this complex [δ-(C_6D_6) 0.93 (3 H, t), 1.38 (3 H, d), 3.97 (2 H, q), 4.33 (1 H, q), 6.92 (9 H, m), 7.4 (6 H, m)] supports the ethyl 2-methylmalonyl structure which was apparently formed according to reaction 4. The solution of this complex
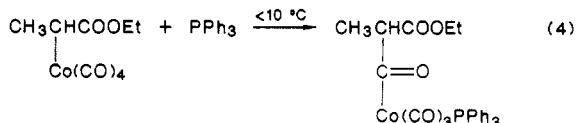

evolved CO above room temperature during which its color turned to pale yellow and new ^1H NMR signals appeared
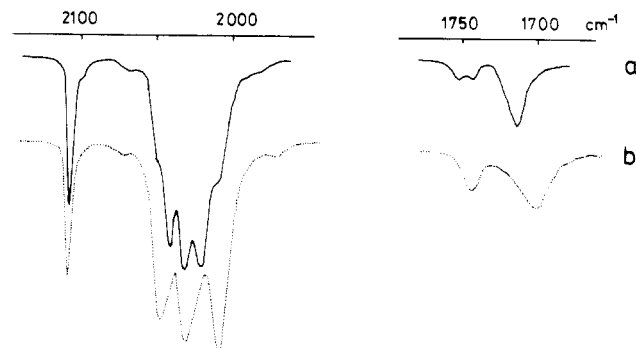
Figure 2. The infrared spectrum in the ν(CO) range of the reaction mixture of ethyl acrylate (0.200 M) and $HCo(CO)_4$ (0.030 M) in the presence 1 bar of CO: (a) after the CO uptake (0.25 mol of CO/mol of $HCo(CO)_4$) practically stopped at 10 °C and $Co_2(CO)_8$ was frozen out at −79 °C; (b) after the foregoing mixture was warmed up to 25 °C and an additional CO uptake (0.42 mol of CO/mol of $HCo(CO)_4$) was obtained. In both spectra the absorptions of ethyl acrylate have been compensated.

at [δ(C_6D_6) 1.08 (3 H, t), 1.75 (3 H, dd, $^4J_{(^1H-^{31}P)}$ = 6 Hz), 3.47 (1 H, dq, $^3J_{(^1H-^{31}P)}$ = 3 Hz), 4.22 (2 H, t), 6.93 (9 H, m), 7.4 (6 H, m)] which confirmed the formation of $EtOC(O)CH(CH_3)Co(CO)_3PPh_3$ according to reaction 5.
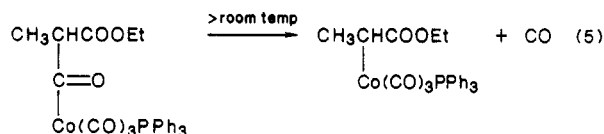
When the reaction of ethyl acrylate and $HCo(CO)_4$ was repeated as above but if after the uptake of 0.25 mol of CO at 10 °C, the reaction mixture was warmed up to 25 °C, an additional CO uptake of 0.42 mol/(mol of $HCo(CO)_4$) occurred. The infrared spectrum of this reaction mixture after $Co_2(CO)_8$ has been frozen out at −79 °C showed ν(CO) bands at 2107 (m), 2045 (s), 2028 (vs), 2007 (vs), 1742 (w), and 1703 (w) cm^{-1} (Figure 2b), characteristic of an acylcobalt tetracarbonyl[9] containing a carboxylic ester group in the organic part of the molecule. On the addition of PPh_3 to the solution CO evolution (0.51 mol/(mol of $HCo(CO)_4$) and the precipitation of a triphenylphosphine derivative resulted. The ^1H NMR spectrum of this complex [δ(C_6D_6) 0.89 (3 H, t), 2.32 (2 H, t), 3.43 (2 H, t), 3.88 (2 H, q), 6.95 (9 H, m), 7.4 (6 H, m)] supports the ethyl succinyl structure which was formed by isomerization, CO uptake, and PPh_3 substitution from (1-(ethoxycarbonyl)-ethyl)cobalt tetracarbonyl according to reactions 6 and 7.
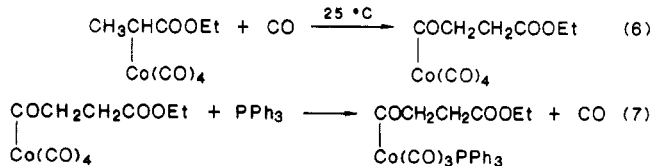
In order to prove the structural change in reaction 6 by an independent way, the reaction mixture was pressurized with H_2. A smooth reduction occurred at room temperature according to reaction 8 and the ethyl 3-formyl-propionate formed could be identified through its 2,4-di-nitrophenylhydrazone derivative [δ(C_6D_6) 0.96 (3 H, t), 2.18 (4 H, m), 3.94 (1 H, q), 6.08 (1 H, t), 7.31 (1 H, d), 7.76 (1 H, dd) 8.77 (1 H, d), 10.32 (1 H, s)].

The concentration of $Co_2(CO)_8$ practically did not influence the rate and the amount of CO uptake in reaction

(8) (a) Galamb, V.; Pályi, G. *Acta Chim. Acad. Sci. Hung.* **1982**, *111*, 131. (b) Pályi, G.; Galamb, V.; Röder, A. *Atti Accad. Sci. Ist. Bologna, Cl. Sci. Fis., Ser.XIII*, **1981**, *VIII*, 67.

(9) Markó, L.; Bor, G.; Almásy, G.; Szabó, P. *Brennst.-Chem.* **1963**, *44*, 184.

$$\underset{\underset{Co(CO)_4}{|}}{COCH_2CH_2COOEt} + H_2 \xrightarrow[\text{100 bar}]{\text{room temp}} \underset{\underset{CHO}{|}}{CH_2CH_2COOEt} +$$

$$Co_2(CO)_8 \quad (8)$$
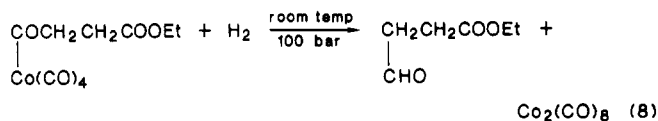
6. The rate of CO uptake was, however, inversely proportional to the CO concentration (Table III).

Similar kinetic and spectroscopic results were obtained also in the case of ethyl crotonate, diethyl fumarate, and diethyl maleate. With the latter two compounds no secondary CO uptake occurred, however. From diethyl maleate a considerable amount of diethyl fumarate was formed during the reaction with HCo(CO)₄.

Discussion

The Co₂(CO)₈-Catalyzed Reaction of HCo(CO)₄ with Ethyl Acrylate. The kinetic behavior described in this work is similar to that already observed for heptene-1 and octene-1 under the same conditions.[5a] On the basis of this analogy, we propose the mechanism represented by Scheme I for the reaction between HCo(CO)₄ and CH₂= CHCOOEt. If k_a is regarded as rate determining, we obtain the following expressions for the rate of CO uptake and ethyl propionate formation:
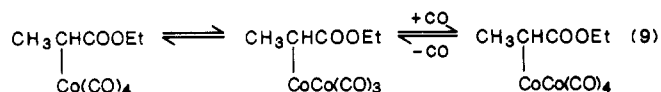
$$r_{CO} = \frac{A \dfrac{k_{CO}}{k_H}[HCo(CO)_4]}{\dfrac{k_{CO}}{k_H}[CO] + [HCo(CO)_4]}$$

$$r_H = \frac{A[HCo(CO)_4]^2[CO]^{-1}}{\dfrac{k_{CO}}{k_H}[CO] + [HCo(CO)_4]}$$

where $A = k_a K_1^{0.5} K_2 [Co_2(CO)_8]^{0.5}[CH_2{=}CHCOOEt]$

The rate constants $k_{obsd} = k_a K_1^{0.5} K_2$ and k_{CO}/k_H according the Scheme I were calculated from the slope and intercept in Figure 3 by plotting the reciprocal initial rates of CO uptake vs. the concentration ratios of CO and HCo(CO)₄ using the experimental points in Tables I and II.

The main difference to earlier findings is that in the case of the olefins investigated in this work during the course of the reaction not an acyl but an alkylcobalt tetracarbonyl accumulates in the product. This we believe is the first convincing evidence for the intermediacy of an alkylcobalt carbonyl in the hydroformylation of an olefin. Apparently the COOEt group stabilizes the carbon–cobalt bond much more in the alkyl than in the acyl complex, and therefore the equilibrium in reaction 9 is shifted to the left side. This is an accordance with the fact that ROOCCH₂Co(CO)₄ type complexes[10] are stable even at room temperature.

$$\underset{\underset{Co(CO)_4}{|}}{CH_3CHCOOEt} \rightleftharpoons \underset{\underset{CoCo(CO)_3}{|}}{CH_3CHCOOEt} \underset{-CO}{\overset{+CO}{\rightleftharpoons}} \underset{\underset{CoCo(CO)_4}{|}}{CH_3CHCOOEt} \quad (9)$$

The alkylcobalt complex can be converted into derivatives of the acylcobalt complex by irreversible reactions running over the corresponding acylcobalt tricarbonyl with HCo(CO)₄, H₂, or PPh₃.

A comparison of the k_{obsd} values in Table IV shows that in analogy to our earlier experiences with different internal and terminal olefins[5] ethyl crotonate and diethyl maleate

(10) (a) Galamb, V.; Pályi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1981**, *209*, 183. (b) Galamb, V.; Pályi, G.; Kajtár, M. *Inorg. Chim. Acta* **1981**, *55*, L113.

Table III. The Rate of CO Uptake (r'_{CO}) and the Amount of Absorbed CO (CO'_{max}) of a Solution of (1-(Ethoxycarbonyl)ethyl)cobalt Tetracarbonyl[a] at Various Conditions

temp, °C	10^2[CO], M	[Co₂(CO)₈], M	$10^6 r'_{CO}$, M·s⁻¹	CO'_{max}[b]
10	0.967	0.100	0.13	
25	0.520	0.002	3.2	0.39
25	1.050	0.002	1.5	0.42
25	2.00	0.002	0.8	
25	45	0.002	0.03[c]	0.02[c]
25	0.480	0.240	4.6	0.49
25	1.050	0.240	2.2	0.43
25	1.98	0.240	0.8	
25	50	0.240	0.01[d]	0.06[d]

[a] Derived from the reaction of ethyl acrylate (0.200 M) and HCo(CO)₄ (0.030 M) in the presence of Co₂(CO)₈ (0.098 M) under CO at 10 °C, reaction interrupted at 0.25 mol of CO uptake per mol of HCo(CO)₄. [b] Mol of CO/mol of HCo(CO)₄. [c] 6% conversion in 5 h, based on the IR spectrum. [d] 20% conversion in 50 h, based on the IR spectrum.

Table IV. The Observed Rate Constant (k_{obsd}) and the Ratio of k_{CO} to k_H in the Co₂(CO)₈-Catalyzed Reaction of HCo(CO)₄ with Different Olefins

olefin	temp, °C	$10^5 k_{obsd}$, M⁻⁰·⁵ s⁻¹	k_{CO}/k_H	ref
allylbenzene	15	2.4	14	5c
1-heptene	15	3.2	18	5a
2-heptene[a]	15	0.31	12	5b
3-heptene[b]	15	0.64	14	5b
cyclohexene	15	0.025	11	5b
ethyl crotonate[c]	10	0.4	3.4	
ethyl acrylate	10	24	5	
diethyl fumarate	10	24	3.1	
diethyl maleate	10	12 ± 3[d]	3.4 ± 1[d]	

[a] 47% trans and 53% cis. [b] 30% trans and 70% cis. [c] Trans. [d] A possible source of deviation is the observed extensive isomerization to diethyl fumarate.
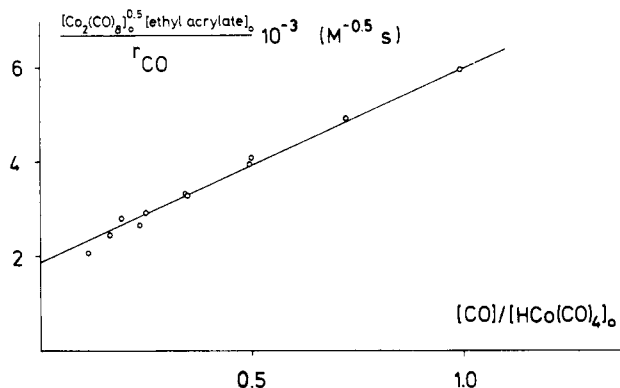
Figure 3. The reciprocal initial rate of CO uptake vs. [CO]/ [HCo(CO)₄]₀ at 10 °C.

are less reactive than ethyl acrylate. Diethyl fumarate, however, reacts with HCo(CO)₄ as fast as ethyl acrylate. For a better understanding of the structure-reactivity patterns in these cases the peculiarities of olefin complex formation and that of hydrogen atom transfer (cf. Scheme I) have to be cleared, however.

The Skeletal Isomerization of (1-(Ethoxycarbonyl)ethyl)cobalt Tetracarbonyl. From earlier studies based on gas chromatographic detection of methyl malonic and succinic acid esters obtained by decomposition of the organocobalt intermediates with iodine + alcohol reagent, it was concluded that the formation of isomeric aldehydes in the reaction of acrylic esters and HCo(CO)₄ proceeds through the corresponding α- and β-(tetracarbonylcobaltio)propionic acid esters.[11,12]

Scheme I

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

$$\cdot Co(CO)_4 + CH_2=CHCOOEt \underset{}{\overset{K_2}{\rightleftharpoons}} \cdot Co(CO)_3(CH_2=CHCOOEt) + CO$$

$$\cdot Co(CO)_3(CH_2=CHCOOEt) + HCo(CO)_4 \xrightarrow[\text{slow}]{k_a} \underset{HCo(CO)_3}{CH_2=CHCOOEt} + \cdot Co(CO)_4$$

$$\underset{HCo(CO)_3}{CH_2=CHCOOEt} \overset{K_3}{\rightleftharpoons} \underset{Co(CO)_3}{CH_3CHCOOEt}$$

$$\underset{Co(CO)_4}{CH_3CHCOOEt} \qquad\qquad (EtOOCCH)(H)Co_2(CO)_7 \\ \qquad\qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\qquad\qquad CH_3$$

$$\underset{COCo(CO)_3}{CH_3CHCOOEt} \qquad EtOOCCH_2CH_3 + Co_2(CO)_8$$

$$\underset{COCo(CO)_4}{CH_3CHCOOEt} \qquad\qquad (EtOOCCHCO)(H)Co_2(CO)_7 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_3$$

$$EtOOCCHCHO + Co_2(CO)_8 \\ \quad | \\ \quad CH_3$$

Scheme II

$$\underset{Co(CO)_4}{CH_3CHCOOEt} \underset{+CO}{\overset{-CO}{\rightleftharpoons}} \underset{Co(CO)_3}{CH_3CHCOOEt} \rightleftharpoons \underset{HCo(CO)_3}{CH_2=CHCOOEt} \overset{slow}{\rightleftharpoons} \underset{(CO)_3CoH}{CH_2=CHCOOEt}$$

$$\Big\downarrow \text{very slow}$$

$$\underset{Co(CO)_4}{OCCH_2CH_2COOEt} \underset{-CO}{\overset{+CO}{\rightleftharpoons}} \underset{Co(CO)_3}{OCCH_2CH_2COOEt} \rightleftharpoons \underset{Co(CO)_4}{CH_2CH_2COOEt} \overset{+CO}{\rightleftharpoons} \underset{Co(CO)_3}{CH_2CH_2COOEt}$$
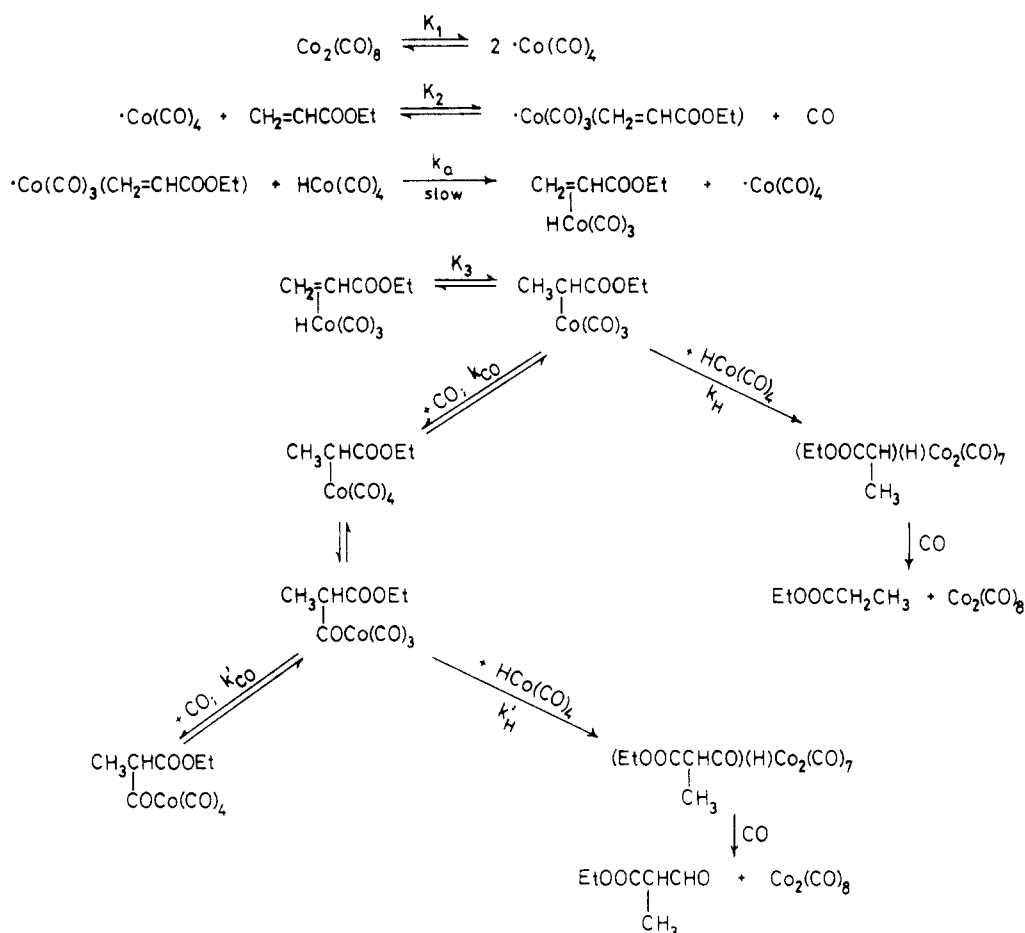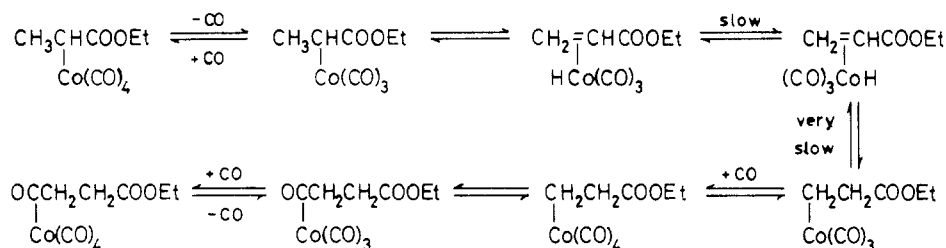
The material balance, spectroscopic evidences, and kinetics of the CO uptake during the skeletal isomerization (reaction 6) observed in our experiments allow a more detailed description of the molecular mechanism of this process according to Scheme II. The negative order in carbon monoxide suggests that tricarbonyl complexes are involved in the slow step.

It should be noted that the reaction sequence depicted in Scheme II does not require $Co_2(CO)_8$ (i.e., $Co(CO)_4$ radical) as a catalyst, in contrast to the reaction between ethyl acrylate and $HCo(CO)_4$ (cf. Scheme I).

The driving force for the isomerization of (1-(ethoxycarbonyl)ethyl)cobalt tetracarbonyl into (3-(ethoxycarbonyl)propionyl)cobalt tetracarbonyl is obviously the increased thermodynamic stability of the latter complex. In this respect the situation is closely analogous to that observed in the case of styrene;[4a] i.e., the branched compound is the kinetically controlled and the straight chain compound the thermodinamically controlled product. A

strong support for this interpretation comes from the observation that under catalytic conditions the formation of ethyl 3-formylpropionate increases with increasing reaction temperature at the expense of the 2-formyl isomer.[2]

Finally it may be pointed out that the reaction of α,β-unsaturated carboxylic acid esters with $HCo(CO)_4$ is analogous to that of aliphatic olefins and $HCo(CO)_4$ in its initial stages (catalysis by $Co_2(CO)_8$),[5] but the isomeric distribution of products is governed by kinetic and thermodynamic factors observed in the reaction of $HCo(CO)_4$ with styrenes.[4a] Apparently all major classes of olefins show individual characteristics in their behavior in the hydroformylation reaction catalytic cycle.

Experimental Section

General Techniques. Infrared spectra were recorded on a Carl Zeiss Jena Ir 75 spectrophotometer. The spectra were calibrated in the $\nu(CO)$ region by recording the gas spectrum of CO and using the known published wawenumbers.[13] NMR

(11) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* 1961, *83*, 4023.
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spectra were recorded with a Tesla BS 487/C 80-MHz spectro-photometer using Me$_4$Si as the internal standard. Analysis of the volatile compounds was performed on an analytical Hew-lett-Packard Model 5830A gas chromatograph using 30-m glass capillary column with 0.15-μm OV-1 stationary phase and *n*-nonane internal standard. All manipulations involving air-sensitive organometallic compounds were carried out by using Schlenk techniques.[14] Reactions above 3-bar pressure were performed with 10-mL samples in a 20-mL stainless-steel rocking autoclave.

Materials. The solvents were dried in the usual way and stored under CO. Commercial ethyl acrylate was freshly distilled under CO. Stock solutions of HCo(CO)$_4$ were prepared in *n*-octane from Co$_2$(CO)$_8$, DMF, and concentrated HCl.[15] The concentration of HCo(CO)$_4$ solutions was determined by 0.1 N alkaline titration at 0 °C under CO. Dicobalt octacarbonyl was doubly recrystallized first from CH$_2$Cl$_2$ and then from *n*-heptane under CO.

Kinetic runs were performed in a gasometric apparatus fitted with a mercury-filled gas burette. A 5-L buffer flask was connected to the leveling vessel of the gas burette and kept at the pressure of the reaction vessel. All parts of the apparatus were thermo-stated (±0.05 °C). 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 the ethyl acrylate into the vigorously stirred solution of HCo(CO)$_4$ and Co$_2$(CO)$_8$. In the case of ethyl (3-(ethoxycarbonyl)propionyl)cobalt tetra-carbonyl formation the reaction was started by injecting freshly warmed up solutions of (1-(ethoxycarbonyl)ethyl)cobalt tetra-carbonyl into the vigorously stirred solvent or into solutions of Co$_2$(CO)$_8$. The initial rate of CO uptake was calculated from the change of gas volume with time.

The PPh$_3$-substituted derivatives were prepared in a ga-sometric apparatus by adding 10% molar excess of PPh$_3$ (based on Co) as a 0.3 M solution in toluene/heptane (1:8, v/v) to the reaction mixture prepared from ethyl acrylate and HCo(CO)$_4$ under CO after the Co$_2$(CO)$_8$ crystals have been removed at –79 °C. Yellow crystals formed within 10 min.

The 2,4-dinitrophenylhydrazone derivatives were prepared by adding 10% molar excess of perchloric acid stabilized 2,4-dinitrophenylhydrazine in water to the reaction mixture followed by cooling overnight in the refrigerator and filtration of the precipitate.

Registry No. HCo(Co)$_4$, 16842-03-8; CH$_2$=CHCOOEt, 140-88-5; ethyl propionate, 105-37-3; ethyl 2-formylpropionate, 27772-62-9; (1-(ethoxycarbonyl)ethyl)cobalt tetracarbonyl, 85421-34-7; (2-(ethoxycarbonyl)propionyl)(triphenyl-phosphine)tricarbonyl cobalt, 104465-48-7; (1-(ethoxycarbonyl)-ethyl)(triphenylphosphine)tricarbonyl cobalt, 104465-49-8; (3-(ethoxycarbonyl)propionyl)cobalt tetracarbonyl, 104465-50-1; (3-(ethoxycarbonyl)propionyl)(triphenylphosphine)tricarbonyl cobalt, 104465-51-2; ethyl 3-formylpropionate, 10138-10-0.

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13C NMR and EHMO Studies on Seyferth's [Co$_3$(CO)$_9$CCO]$^+$ Cluster: To Bend or Not To Bend

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Variable-temperature 13C NMR studies on [Co$_3$(CO)$_9$CCO]$^+$ and its Ph$_3$P-substituted analogue are described. At –110 °C, the 125.7-MHz 13C NMR spectrum of [Co$_3$(CO)$_9$CCO]$^+$ exhibits a 3:6 pattern for the cobalt carbonyls. This is interpreted in terms of a tilted (C_s) geometry for the ketenylidene fragment rather than a perpendicular (C_{3v}) arrangement. It is proposed that [(Ph$_3$P)Co$_3$(CO)$_8$CCO]$^+$ and [CpMo-Co$_2$(CO)$_8$CCO]$^+$ also have related structures in which localized Co(CO)$_3$ rotation cannot be slowed on the NMR time scale. Extended Hückel molecular orbital calculations consistently found the C_s geometry to be the most stable for [Co$_3$(CO)$_9$CCO]$^+$ and for the related molecule [Fe$_3$(CO)$_9$CCO]$^{2-}$, with the ketenylidene fragment leaning toward a metal vertex. The energy variation was found to be small over a large range of bending angles, in contrast with the [Co$_3$(CO)$_9$CCH$_2$]$^+$ cluster. The difference between this latter cation and the ketenylidene clusters is analyzed.

Introduction

Among the more interesting systems which have emerged from studies on metal clusters are those con-taining the ketenylidene ligand, C=C=O, which are be-lieved to be models for the reduction of CO on metal surfaces.[1] The first reported synthesis[2] of such a system described the tricobalt acylium ion 1, and since that time the chemistry of this cluster has been extensively devel-oped.[3] Nevertheless, despite numerous attempts to obtain good crystallographic data,[4] the structure of 1 is still a

matter of conjecture and both the linear (C_{3v}) geometry, 1a, and bent (C_s) conformation, 1b, are viable candidates. The infrared spectroscopic data[5] militate against structures involving bridging carbonyls between the metal vertices.

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