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Note

Kinetics and mechanism of the methanolysis of acetylcobalt tetracarbonyl ☆

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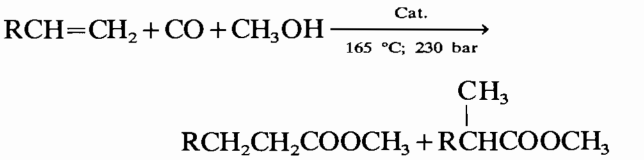
Abstract

The rate of acetylcobalt tetracarbonyl methanolysis between 40 and 60 °C is first-order with respect to the acetylcobalt tetracarbonyl concentration and independent of the carbon monoxide concentration. The reaction is susceptible to both acid and base catalysis. Nucleophilic substitution of $Co(CO)_4$ on the acyl carbonyl-carbon by methanol is the most probable pathway.

Keywords: Kinetics and mechanism; Methanolysis; Cobalt complexes; Acetyl complexes; Carbonyl complexes

1. Introduction

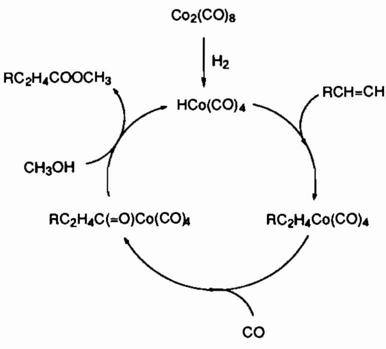
Carboxylic acid methylesters are prepared commercially by the cobalt-catalyzed methoxycarbonylation of the carbon–carbon double bond of olefins [1] and diolefins [2]. Nitrogen bases such as pyridine serve as co-catalysts in the synthesis.



$$RCH{=}CH_2 + CO + CH_3OH \xrightarrow[165\ °C;\ 230\ bar]{Cat.} RCH_2CH_2COOCH_3 + RCH(CH_3)COOCH_3$$

Methanolysis of the acylcobalt tetracarbonyl complex is the product-forming step in the assumed catalytic cycle [3] (Scheme1), and probably this reaction is the rate-determining step.

The formation of methyl acetate and the corresponding carbonylcobaltate anion has been demonstrated in the reaction of $CH_3C(=O)Co(CO)_4$, $CH_3C(=O)Co(CO)_3PPh_3$ and $CH_3C(=O)Co(CO)_2[P(OCH_3)_3]_2$ with $NaOCH_3$ [4,5] and in the reaction of $CH_3C(=O)Co(CO)_4$ with CH_3OH in the presence of pyridine [6].



Scheme 1.

In order to learn more about the mechanism of the reaction we have studied the products and the rates under various experimental conditions using $CH_3C(=O)Co(CO)_4$, $^nPrC(=O)Co(CO)_4$ and $^iPrC(=O)Co(CO)_4$ (prepared from the corresponding ketene and $HCo(CO)_4$ [7]) as model complexes.

2. Results

We have found that solutions of $CH_3C(=O)Co(CO)_4$ in methanol give at 25 °C in a reaction time of 1 day varying amounts of methyl acetate and acetaldehyde dimethyl acetal as the only organic products and $[Co(CO)_4]^-$ and Co^{2+} as the cobalt-containing byproducts.

☆ Dedicated to our friend Professor György Bor on the occasion of his 70th birthday in recognition of his pioneering work in metal carbonyl chemistry.

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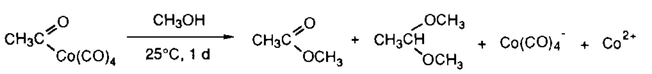


$CH_3C(=O)Co(CO)_4 \xrightarrow[25^\circ C,\ 1\ d]{CH_3OH} CH_3C(=O)OCH_3 + CH_3CH(OCH_3)_2 + Co(CO)_4^- + Co^{2+}$

On the addition of a nitrogen base, or of HCl, the rate of conversion of $CH_3C(=O)Co(CO)_4$ increases (Fig. 1).

The rate of the reaction was measured by two independent methods. IR spectroscopy was applied to follow the decrease of intensity of the highest ν(CO) band of $CH_3C(=O)Co(CO)_4$ at 2106 cm^{-1} in the IR spectrum. NMR spectroscopy was used to follow the decrease of the methyl proton signal of $CH_3C(=O)Co(CO)_4$ at 2.74 ppm or the increase of the acyl-methyl proton signal of methyl acetate at 2.00 ppm in the ^1H NMR spectrum using CD_3OD as the solvent. Under the same experimental conditions identical rates were obtained by following the progress of the reaction using IR and NMR spectroscopy. The rate of acetylcobalt tetracarbonyl methanolysis was found to be first-order with respect to the acetylcobalt tetracarbonyl concentration and independent of the carbon monoxide concentration. Measurements under various experimental conditions using CD_3OD as the solvent have shown that the CO concentration influences only the ratio of methyl acetate and acetaldehyde dimethyl acetal in the product. Under argon atmosphere at 45 °C, a mixture of 64% CH_3COOCD_3 and 36% $CH_3OCD(OCD_3)_2$ was formed in 7 h. The same experiment under 3 bar CO pressure gave CH_3COOCD_3 in quantitative yield.

Table 1 shows the observed pseudo-first-order rate constants of the reaction between 40 and 60 °C, which define $\Delta H^{\ddagger}$ (25 °C) = 23.7 ± 0.3 Kcal mol^{-1} and $\Delta S^{\ddagger}$ (25 °C) = −0.4 ± 0.5 cal mol^{-1} K^{-1}.

Comparison of the rates of acylcobalt tetracarbonyl methanolysis in the case of acetyl-, n-butyryl- and isobutyrylcobalt tetracarbonyl (Fig. 2) shows that acetylcobalt tetracarbonyl is more reactive than the two other acyl complexes, and the n-butyryl complex is a little more reactive than the isobutyryl one.

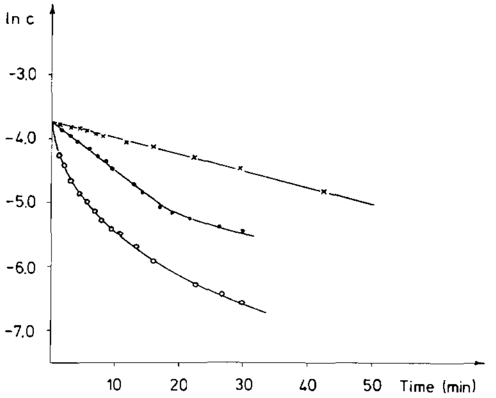


Fig. 1. The observed change of concentration of $CH_3C(=O)Co(CO)_4$ (c, mol/l) in methanol solution at 50 °C under CO at atmospheric pressure: (×) in the absence of HCl and $^iPr_2EtN$; (●) in the presence of HCl ($CH_3C(=O)Co(CO)_4$:HCl = 1.08:1); (○) in the presence of $^iPr_2EtN$ ($CH_3C(=)Co(CO)_4$:$^iPr_2EtN$ = 1:1.1).

Table 1
The observed pseudo-first-order rate constant of the methanolysis of acetylcobalt tetracarbonyl at different temperatures and carbon monoxide concentrations

T (°C)	10^2 $[CH_3C(=O)Co(CO)_4]_0$ (M)	10^3 [CO][a] (M)	10^4 k_1 (s^{-1})
40	2.2	5.70	1.4
45	2.2	4.91	2.3
50	2.3	4.00	4.4
50	2.2	3.00	4.6
50	2.2	1.00	4.5
55	2.3	2.78	8.0
60	2.0	1.35	14.3

[a] Calculated from the pCO and the solubility of CO in methanol [8].

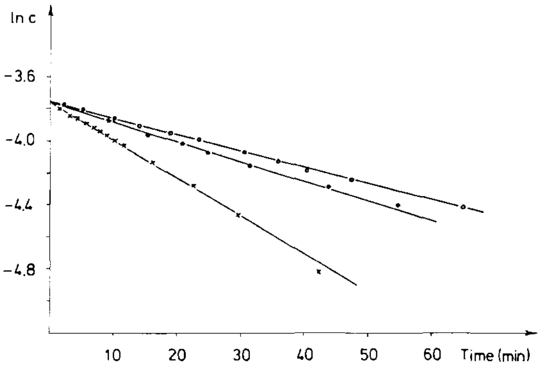
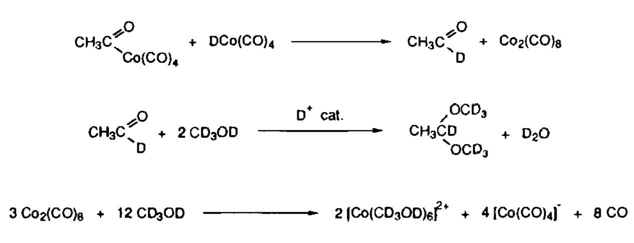


Fig. 2. The observed change of concentration of $RC(=O)Co(CO)_4$ (c, mol/l) in methanol solution at 50 °C under CO at atmospheric pressure: (×) $R = CH_3$; (●) $R = CH_3CH_2CH_2$; (○) $R = (CH_3)_2CH$.

3. Discussion

The appearance of $CH_3CD(OCD_3)_2$ in experiments carried out in CD_3OD under low pCO is obviously the consequence of the intermediate formation of $CH_3C(=O)D$ from $CH_3C(=O)Co(CO)_4$ and $DCo(CO)_4$, which in turn rapidly converts into dimethylacetal in the acidic solution. The other product of this acyl-cleavage reaction is $Co_2(CO)_8$ which gives rise to Co^{2+} by the disproportionation reaction with methanol [9].



$CH_3C(=O)Co(CO)_4 + DCo(CO)_4 \longrightarrow CH_3C(=O)D + Co_2(CO)_8$

$CH_3C(=O)D + 2CD_3OD \xrightarrow{D^+\ cat.} CH_3CD(OCD_3)_2 + D_2O$

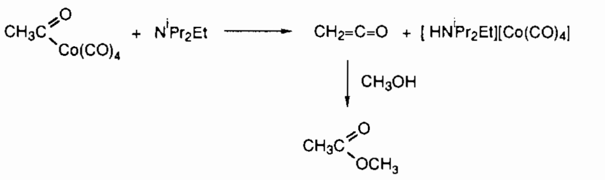
$3Co_2(CO)_8 + 12CD_3OD \longrightarrow 2[Co(CD_3OD)_6]^{2+} + 4[Co(CO)_4]^- + 8CO$

At higher pCO the methanolysis reaction prevails over the cleavage of $CH_3C(=O)Co(CO)_4$ by $DCo(CO)_4$ because the rate of methanolysis is independent of the CO concentration whereas the rate of the cleavage reaction is inversely proportional to the CO concentration [10].

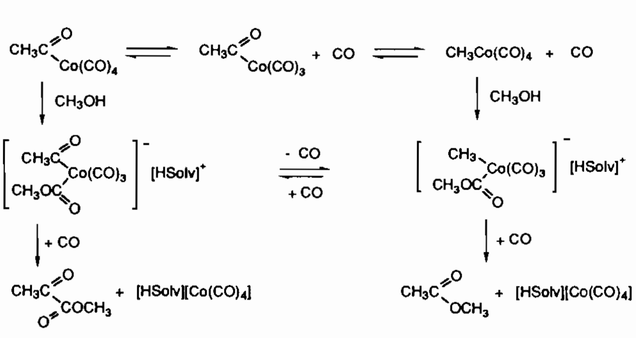
Different CO-independent pathways may account for the formation of methyl acetate from acetylcobalt tetracarbonyl in methanol. Three of them are depicted in Schemes 2, 3 and 4.

Elimination of ketene from acetylmetal compounds has been demonstrated in the case of the unstable $[CH_3C(=O)Ru(CO)_2(triphos)]^+$ complex [11]. In the case of acetylcobalt tetracarbonyl, however, a pathway according to Scheme 2 can be excluded because in CD_3OD solution both in the presence and in the absence of N^iPr_2Et, $CH_3C(=O)OCD_3$ is formed quantitatively with no deuterium incorporation into the acyl-methyl, which might be expected if the reaction went through a ketene intermediate.

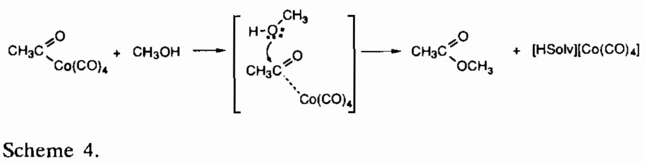
As further alternatives a rate-determining nucleophilic attack of methanol (or methoxy ion) on the carbon atom of a terminal CO ligand (Scheme 3) or on the acyl carbonyl of $CH_3C(=O)Co(CO)_4$ (Scheme 4) can be envisaged. In the first case the reaction would give methoxycarbonylacetylcobalt tricarbonyl, which in the presence of CO could either decompose to methyl pyruvate or decarbonylate first to a methoxycarbonylmethylcobalt tricarbonyl complex and then decompose to methyl acetate.



Scheme 2.

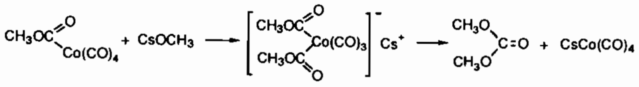


Scheme 3.



Scheme 4.

Such a nucleophilic attack of the methoxy ion on a coordinated CO ligand has been established already as the source of various $[XYCo(CO)_3]^-$ complexes, where X and Y are an alkyl, alkoxy, acyl or alkoxyacyl group [12,13]. A bismethoxycarbonylcobalt complex from the reaction of $CH_3OC(=O)Co(CO)_4$ and cesium methoxide was recently isolated and characterized by X-ray structure determination and was found to afford dimethyl carbonate in a CO-retarded decomposition [14].



The analogous decomposition of the intermediate methoxycarbonylacetylcobalt complex in Scheme 3 may explain the formation of methyl acetate. The formation of pyruvate [15] and oxalate [16] by the reductive elimination of the corresponding X and Y groups in similar iron complexes has been described recently. Methylpyruvate, however, could not be detected in our case among the reaction products by IR spectroscopy.

Scheme 4 shows the case of the nucleophilic attack of methanol on the acyl carbonyl-carbon. Based on all the experimental evidence available we regard this reaction pathway as the most probable one.

In accord with the observed effect of $^iPr_2EtN$ and HCl on the rate of the reaction this mechanism is expected to be susceptible to both acid and base catalysis. Deprotonation of the attacking methanol by another molecule of methanol (in a way similar to that in the well established acyl halide alcoholysis [17,18]) or by an added nitrogen base will lead to the methoxide anion, a powerful nucleophile. On the other hand, hydrochloric acid is also expected to increase the reaction rate because the protonation of the acetyl oxygen increases the electrophilic character of the acetyl carbonyl carbon atom. The order of reactivity in the case of different acylcobalt tetracarbonyls also supports the role of the electrophilic character of this carbon atom in determining the rate of the reaction.

4. Experimental

4.1. *Measurement of the rate of methanolysis of acetylcobalt tetracarbonyl using IR spectroscopy*

To 9.0 ml vigorously stirred methanol at the chosen temperature under CO in a thermostatted reactor, equipped with a reflux-condenser and a septum-closed injection-port, 0.9 ml of a 0.26 M n-heptane solution of $CH_3C(=O)Co(CO)_4$ [7] was added. Liquid samples from the reaction mixture were transferred in various intervals by a TLL-type syringe through a three-way stopcock (Hamilton) and Teflon tubing into a 0.21 mm solution cell with CaF_2 windows and the IR spectrum was recorded at room temperature in the ν(CO) range on a Specord IR 75 (Carl Zeiss, Jena) spectrometer. The concentration of $CH_3C(=O)Co(CO)_4$ in the sample was calculated from the highest ν(CO) band at 2106 cm^{-1} using the experimental molar absorbance, ϵ_M^{2106} ($CH_3C(=O)Co(CO)_4$) = 1011.9 cm^2 $mmol^{-1}$ (in methanol). In the case of $CH_3CH_2CH_2C(=O)Co(CO)_4$ and $(CH_3)_2CHC(=O)Co(CO)_4$ 0.45 M stock solutions in n-octane and experimental molar absorbances ϵ_M^{2105} ($CH_3CH_2CH_2C(=O)Co(CO)_4$, methanol) = 952.4 cm^2 $mmol^{-1}$ and ϵ_M^{2105} ($(CH_3)_2CHC(=O)Co(CO)_4$, methanol) = 1142.8 cm^2 $mmol^{-1}$ were used, respectively.

The effect of hydrochloric acid and diisopropylethylamine on the rate of methanolysis was checked by using solutions of dry HCl and freshly distilled $^iPr_2EtN$ in methanol under CO.

The effect of carbon monoxide was checked by running the experiments under CO and under different mixtures of Ar and CO.

4.2. Identification of the products and measurement of the rate of methanolysis of acetylcobalt tetracarbonyl using NMR spectroscopy

To 0.46 ml of CD_3OD (Aldrich) in a 5 mm 524-JY-7 NMR tube (Wilmad) at −79 °C, 2.5 μl of neat $CH_3C(=O)Co(CO)_4$ were added, and the methanolysis reaction was started by immersing the tube in a water bath at 45 °C with occasional shaking. The ^1H NMR spectrum of the reaction mixture was registered at 45 °C at various intervals on a Varian Unity 300 spectrometer. $CH_3C(=O)Co(CO)_4$, $CH_3C(=O)OCD_3$ and $CH_3CH(OCD_3)_2$ gave sharp methyl resonances at 2.74, 2.00 and 1.26 ppm (δ), respectively.

The effect of carbon monoxide on the product composition and the rate of methanolysis was checked by running the above measurement under Ar, and under CO (1 and 3 bar).

The effect of diisopropylethylamine was studied by adding neat $^iPr_2EtN$ to the reaction mixture at the beginning of the experiment.

Acknowledgements

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