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The equilibrium between acetyl- and methylcobalt tetracarbonyl ☆

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Abstract

The equilibrium between acetylcobalt tetracarbonyl on one side and methylcobalt tetracarbonyl and carbon monoxide on the other has been determined in the 0–100 °C temperature range. The decarbonylation of acetylcobalt tetracarbonyl is endothermic ($\Delta H = 11.2 \pm 0.6$ Kcal mol^{-1}) and is accompanied by a positive entropy change ($\Delta S = 19.5 \pm 2.0$ e.u.).

Keywords: Equilibrium study; Cobalt complexes; Acetyl complexes; Methyl complexes; Carbonyl complexes

1. Introduction

The insertion of carbon monoxide into the carbon–metal bond of alkylmetal carbonyls to form the corresponding acyl derivatives is one of the most important and most investigated organometallic reactions [1]. The interest in this reaction stems to a large extent from the fact that it is one of the essential steps of all organic carbonylations catalyzed by metal carbonyls including the most important one, the hydroformylation of olefins [2].

The chemistry of alkyl- and acylcobalt carbonyls, including their carbonylation and decarbonylation, respectively, has been intensively investigated in recent years [3]. It has been shown that the CO group which is inserted into the cobalt–carbon bond originates from the coordination sphere of the cobalt atom [4] and that the reaction is reversible [4–7].

The position of this equilibrium strongly depends on the structure of the alkyl group. With the exception of $MeCo(CO)_4$ [8,9], alkylcobalt tetracarbonyls with simple aliphatic alkyl groups could not be isolated up till now because they spontaneously insert carbon monoxide and are transformed quantitatively into the corresponding acyl complexes [2,10]. The stability of $RCo(CO)_4$ complexes against CO insertion increases with increasing electron-withdrawing character of the R group. If R is a (substituted) benzyl group the carbonylation–decarbonylation reaction can be easily pushed into either direction by slight modifications of temperature and CO pressure [4–7]. The complexes with an R group of more electron-withdrawing character like fluorinated alkyl [11–14], $ClCH_2$ [6], $HOCH_2$ [7], $ROOCCH_2$ [15], $MeOOCCH(CH_2COOMe)$ [16], and η^1-[η^6-(4-$MeC_6H_4CH_2$)$Cr(CO)_3$] [5] could be isolated and the structure of the last one could even be determined by X-ray crystallography.

Despite this large amount of qualitative information, however, no quantitative data are available on an alkylcobalt–acylcobalt equilibrium. We now report our results on the equilibrium reaction (1).

$$CH_3COCo(CO)_4 \rightleftharpoons CH_3Co(CO)_4 + CO \qquad (1)$$

2. Results and discussion

The decarbonylation of acetylcobalt tetracarbonyl dissolved in n-octane under Ar in a closed system was followed between 0 and 100 °C by three independent experimental methods: (a) measurement of the amount of CO evolved, (b) the IR, and (c) the ^1H NMR spectrum of the solution. However, because above 60 °C decomposition already sets in and acetone was formed in increasing amounts (as shown by the NMR spectra), only the results obtained in the temperature range between 0 and 60 °C can be taken into consideration.

The equilibrium constants at different temperatures as calculated from the experimental results are shown in Fig. 1. The straight line best accommodating the most reliable experimental points gives the following thermodynamic values for reaction (1): $\Delta H = 11.2 \pm 0.6$ Kcal mol^{-1} and $\Delta S = 19.5 \pm 2.0$ e.u. This means, that

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☆ 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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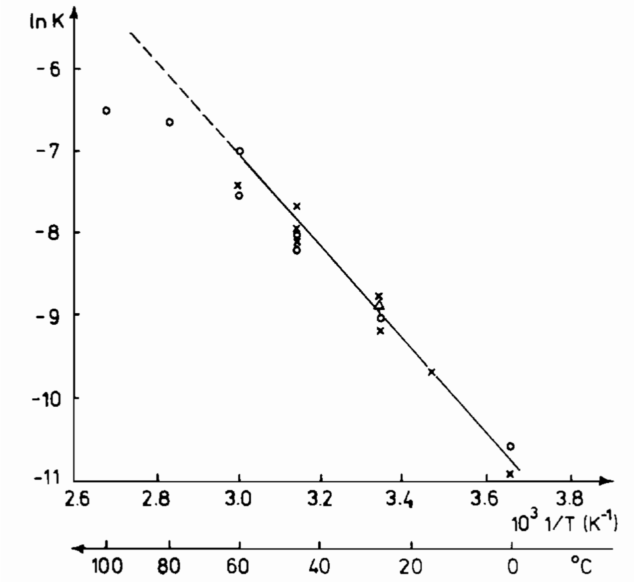

Fig. 1. Equilibrium constant of reaction (1) at different temperatures. Experimental points obtained from: △, CO evolution; ×, IR spectroscopy; ○, ^1H NMR spectroscopy.

the decarbonylation reaction is endothermic (therefore favored by increasing temperatures) and is accompanied by an increase in entropy (which one would expect from the stoichiometry of the reaction).

As can be seen from Fig. 1, the equilibrium constant of reaction (1) at 25 °C is approximately 10^{-4} mol l^{-1}. Considering that the solubility of CO in saturated alkanes at 1 bar is of the order of 10^{-2} mol l^{-1} [17], the equilibrium solution of the two complexes under such conditions will be composed of 99% of the acetyl and only 1% of the methyl complex. One semiquantitative observation has been mentioned in the literature [5] which states that at room temperature and atmospheric pressure under CO a solution of benzylcobalt tetracarbonyl and phenylacetylcobalt tetracarbonyl contains about equal amounts of the two complexes. This means that the equilibrium constant of reaction (2)

$$PhCH_2COCo(CO)_4 \rightleftharpoons PhCH_2Co(CO)_4 + CO \qquad (2)$$

at room temperature is about 10^{-2} mol l^{-1}. These numbers are in accordance with the experimental observations, mentioned in Section 1, that the carbonylation–decarbonylation equilibrium is shifted towards the insertion of carbon monoxide if the electron-donating character of the organic group increases. Considering that among the simple alkyl groups methyl is the least electron-donating it is well understandable that the reaction of $HCo(CO)_4$ with aliphatic olefins the intermediate alkylcobalt tetracarbonyls can never be observed; the reaction product always contains only the corresponding acyl complexes [2,10].

3. Experimental

3.1. Measurement of the amount of CO evolved in the decarbonylation of acetylcobalt tetracarbonyl

To 4.84 ml of vigorously stirred n-octane at 25 °C under Ar in a thermostatted reactor of 80 ml total volume, connected through a condenser to a mercury-filled gas burette, both thermostatted to 13 °C, 0.16 ml of a 0.625 mol l^{-1} n-octane solution of $CH_3COCo(CO)_4$ [18] was added by a TLL-type syringe (Hamilton). A rapid gas volume change occurred with an initial rate of approximately 1.56 ml/min which stopped in about 90 s at 1.16 ml. From these data $K = [CH_3Co(CO)_4]_{liq}[CO]_{liq}/[CH_3COCo(CO)_4]_{liq} = 1.40 \times 10^{-4}$ mol l^{-1} for the equilibrium constant and $k = 1.0 \times 10^{-2}$ s^{-1} for the initial rate of decarbonylation was calculated.

3.2. Measurement of the equilibrium concentration of acetylcobalt tetracarbonyl using IR spectroscopy

The liquid from the above equilibrium reaction mixture was transferred by a TLL-type syringe through a three-way stopcock and Teflon tubing into a 0.10 mm solution cell with CaF_2 windows and the IR spectrum was recorded in the ν(CO) range on a Specord IR 75 (Carl Zeiss, Jena) spectrometer. Then the liquid was exposed to carbon monoxide by means of a CO-filled 10 ml TLL-type syringe and the IR spectrum of this solution was recorded. The first spectrum showed the bands of acetylcobalt tetracarbonyl and methylcobalt tetracarbonyl partially superposed with the exception of the well separated acetyl ν(CO) band at 1719 cm^{-1} ($CH_3COCo(CO)_4$ $\epsilon_M^{1719} = 1650$, $\epsilon_M^{2044} = 2700$, $\epsilon_M^{2103} = 1150$ cm^2 $mmol^{-1}$ in n-octane). The second spectrum showed only the bands of acetylcobalt tetracarbonyl with absorbances corresponding to the total cobalt concentration. From the absorbance difference of the acetyl ν(CO) band of the two spectra the equilibrium concentration of acetylcobalt tetracarbonyl was calculated. Using this value, the known total cobalt concentration, and the gas and liquid phase volumes, a value of $K = 1.0 \times 10^{-4}$ mol l^{-1} was calculated for the equilibrium constant.

3.3. Measurement of the equilibrium concentration of acetylcobalt tetracarbonyl and methylcobalt tetracarbonyl using NMR spectroscopy

To 0.65 ml of d_{18}-octane (Aldrich) under Ar in a 5 mm 507-JY-7 NMR tube (Wilmad) (total volume 2.82 ml) at −10 °C, 60 μl of a 1.44 M d_{18}-octane solution of $CH_3COCo(CO)_4$ (prepared by mixing 230 μl neat acetylcobalt tetracarbonyl with 750 μl d_{18}-octane in a 1 ml V-shaped vial and closed by a mininert valve) was added by using a cold (−10 °C) 710 SN-type syringe. The tube was closed and held in a water bath at 25 °C with occasional shakings for 5 min before running the ^{1}H NMR experiment at 25 °C on a Varian Unity 300 spectrometer. The spectrum showed sharp resonances of the methyl protons of acetylcobalt tetracarbonyl and methylcobalt tetracarbonyl at 2.70 and 1.06 ppm (δ), respectively. From the known total cobalt concentration, the measured ratio of the different methyl protons, and the size of the tube, the equilibrium constant was calculated as $K = 1.18 \times 10^{-4}$ mol l^{-1}. The same sample was used for measurements at 0, 45 and 60 °C. Repeating at the end the measurement at 25 °C the calculated equilibrium constant was practically the same as at the beginning. In experiments performed at 80 and 100 °C, however, the methyl resonance of acetone appeared at 2.02 ppm. At 100 °C about 50% of the acetylcobalt tetracarbonyl decomposed in 60 min into acetone and a mixture of $Co_2(CO)_8$ and $Co_4(CO)_{12}$.

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