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Cleavage of Co–C and Co–Co Bonds by Hydrogen Halides. Reaction of $(CH_3)_2CHC(O)Co(CO)_4$, $Co_2(CO)_8$, $Co_2(CO)_7PPh_3$ and $Co_2(CO)_6(PBu^n_3)$ with HX (X = Cl, I)

ISTVÁN KOVÁCS, FERENC UNGVÁRY and LÁSZLÓ MARKÓ

Institute of Organic Chemistry, University of Veszprém, 8201 Veszprém, Hungary

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There are suggestions in the literature for the application of the cobaltcarbonyl–hydrochloric acid system for the conversion of α,β-unsaturated nitriles into saturated aldehydes [1] and for the stoichiometric hydroformylation and hydrogenation of olefins [2], alkyl- and benzyl-halides [3]. Very little is known, however, about the role of hydrochloric acid in these reactions. This prompted us to investigate the reaction of hydrogen halides with some carbonyl cobalt complexes. In the case of $EtOC(O)Co(CO)_3L$ ($L = PPh_3$, $P(OPh)_3$) it was already reported that the reaction with HCl at −50 °C gave EtOH and the unstable $[Co(CO)_4L]Cl$ as products [4].

Experimental

All manipulations were carried out using Schlenk techniques [5].

Reaction of Isobutyrylcobalt Tetracarbonyl (1) [6] with HCl

To a stirred solution of dry hydrogen chloride (3.0 mmol) in diethyl ether (6.8 ml) at 25 °C a solution of **1** (1.0 mmol) in n-heptane (3.2 ml) was added under an atmosphere of argon. A rapid initial gas evolution and a slow $CoCl_2$ precipitation from the green solution occurred. After 1.5 h reaction time the infrared spectrum of the solution showed bands characteristic for $Co_2(CO)_8$ (traces), $HCo(CO)_4$ and an aldehyde. Addition of a 20% perchloric acid stabilized solution of 2,4-dinitrophenylhydrazine (1.0 mmol) in water (27 ml) gave the 2,4-dinitrophenylhydrazone of isobutyraldehyde (identified by its ^1H NMR spectrum) in 90% isolated yield.

Reaction of Dicobalt Octacarbonyl (2) with HCl

To a stirred solution of dry hydrogen chloride (0.2 mmol) in diethyl ether (4.5 ml) at 25 °C a solution of **2** (0.1 mmol) in n-heptane (0.5 ml) was added under carbon monoxide at atmospheric pressure. Gas evolution and the formation of a blue precipitate started immediately. In 0.5 h 0.30 mmol gas evolved. Infrared analysis of the solution showed the presence of $HCo(CO)_4$ (0.13 mmol). The concentration of $HCo(CO)_4$ was calculated from the spectrum using the absorbancies of $HCo(CO)_4$ in ether–heptane 9:1 solution at 2116 cm^{-1} ($\epsilon_M = 280$ mmol cm^{-2}). The precipitate was isolated after evaporating the solvent in vacuum at room temperature and was found to be identical with an authentic sample of $CoCl_2$.

Kinetic Runs

These were performed in a thermostated glass reactor connected to a gas burette. The reaction was followed by gas evolution and by infrared spectroscopy, measuring the decrease in absorbancies of the $\nu(C{=}O)$ band of **1** at 2104 cm^{-1} for reaction (1) and of the bridging $\nu(C{=}O)$ band of $Co_2(CO)_8$ at 1857 cm^{-1} for reaction (2).

Results

We found that **1** and **2** react smoothly with hydrochloric acid or with hydrogen iodide at 25 °C in heptane–diethylether solvent mixtures according to eqns. (1) and (2).

$$\underset{\mathbf{1}}{4(CH_3)_2CHC(O)Co(CO)_4} + 4HX \longrightarrow 4(CH_3)_2CHCHO + Co_2(CO)_8 + 2CoX_2 + 8CO \quad (1)$$

$$\underset{\mathbf{2}}{3Co_2(CO)_8} + 4HX \longrightarrow 4HCo(CO)_4 + 2CoX_2 + 8CO \quad (2)$$

In the case of hydrogen iodide the intermediacy of iodocobalt tetracarbonyl [7] could be detected by infrared spectroscopy at −40 °C (Table I).

Phosphine substituted derivatives gave similar results, but their reactivity towards hydrogen halides was less than that of the unsubstituted compounds (Table II). Low temperature (−40 °C) infrared studies proved the presence of $XCo(CO)_3L$ type intermediates ($X = Cl$, I and $L = PBu^n_3$, PPh_3) in both reactions.

Kinetic studies showed that carbon monoxide has an inhibiting effect on the rates and that the reactions are first order in hydrogen halide. Reaction (1) was first order in **1** and reaction (2) was half order in **2**.

No effect on the rate of reaction (1) was found in the presence of trityl radical, isobutyraldehyde, cobalt(II) chloride and water.

These observations suggest that the first step in reaction (1) may be the oxidative addition of

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TABLE I. IR Spectroscopically Identified Products Resulting from Solutions of Different Cobalt Carbonyl Complexes in a 9:1 *v*/*v* Mixture of Diethylether and n-Heptane under Dry Hydrogen Halide Atmosphere at −40 °C in 5 min Reaction Time

Cobalt complex	HX	Products
1	HCl	$(CH_3)_2CHCHO$, $HCo(CO)_4$
1	HI	$(CH_3)_2CHCHO$, $ICo(CO)_4$
$(CH_3)_2CHC(O)Co(CO)_3PPh_3$	HCl	$(CH_3)_2CHCHO$, $ClCo(CO)_3PPh_3$
2	HCl	$HCo(CO)_4$
2	HI	$HCo(CO)_4$, $ICo(CO)_4$
$Co_2(CO)_7PPh_3$	HCl	$HCo(CO)_3PPh_3$
$Co_2(CO)_6(PBu^n_3)_2$	HCl	$HCo(CO)_3PBu^n_3$, $ClCo(CO)_3PBu^n_3$
$Co_2(CO)_6(PBu^n_3)_2$	HI	$HCo(CO)_3PBu^n_3$, $ICo(CO)_3PBu^n_3$

TABLE II. Initial Rates[a] (r_0) and the Achieved Conversion[b] in the Reaction of Different Cobalt Carbonyl Complexes with Hydrogen Chloride at 25 °C in a 9:1 *v*/*v* Mixture of Diethylether:n-Heptane at Various Conditions. Initial Concentrations: $[\text{Cobalt Complex}]_0 = 0.02$ M, $[HCl]_0 = 0.04$ M. Total Pressure = 1 bar

Cobalt complex	Atmosphere[c]	$10^6\ r_0$ (M s^{-1})	Time (h)	Conversion (%)
1[d]	CO	22	24	49
1	CO	112	1.5	28
1	Ar	154	1.5	86
$(CH_3)_2CHC(O)Co(CO)_3PPh_3$	CO		24	<5
2[d]	CO	8	0.5	20
2	CO	318	0.5	100
2	Ar	353	0.5	100
$Co_2(CO)_7PPh_3$	Ar	2[b]	1.5	54
$Co_2(CO)_6(PBu^n_3)_2$	Ar		17	<5

[a]Based on the initial rate of CO evolution. [b]Based on the decrease of absorbance of the starting complex in the IR spectrum. [c]At the start of the experiment. [d]In a 1:9 = diethylether:n-heptane *v*/*v* mixture.

hydrogen halide and that the resulting adduct is subsequently transformed into aldehyde and halogeno cobalt tetracarbonyl. The latter complex is unstable and disproportionates into cobalt(II) halide and 2 accompanied by carbon monoxide evolution.

The observed half order in 2 for reaction (2) suggests that in this case tetracarbonyl cobalt radical may be formed in a fast thermal preequilibrium reaction which then reacts in a slow step with the hydrogen halide. The inhibiting effect of CO suggests that it is perhaps the $^{\cdot}Co(CO)_3$ radical which actually reacts with HX. Consecutive fast steps lead finally to $HCo(CO)_4$, CoX_2 and CO. A similar mechanism has been found for the photochemical reaction of HCl with $Mn_2(CO)_8L_2$ ($L = PBu^n_3$, $P(OEt)_3$) complexes [8].

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