Hydrogenations with Cobalt Hydrocarbonyl

RICHARD W. GOETZ AND MILTON ORCHIN

Department of Chemistry, University of Cincinnati, Cincinnati 21, Ohio

Received April 12, 1962

Although examples of hydrogenation of organic compounds under conditions of the oxo process are well documented,[1-3] relatively little has been published concerning reduction with cobalt hydrocarbonyl at room conditions other than hydrogenolysis of benzyl type alcohols.[4] We wish to report here the stoichiometric reduction of a variety of compounds (Table I) achieved by cobalt hydrocarbonyl at 25° and one atmosphere total pressure.

The reductions proceed under either a hydrogen or nitrogen atmosphere but an atmosphere of carbon monoxide is beneficial because it retards the decomposition of hydrocarbonyl.

TABLE I

HYDROGENATIONS WITH $HCo(CO)_4$

Compound	Ratio, moles compd./$HCo(CO)_4$	Time, hr.[a]	Products	Yield, %[b]
n-Butyraldehyde	10	4	*n*-Butyl alcohol	10
n-Hexaldehyde	10	3.5	*n*-Hexyl alcohol	10
Benzaldehyde	10	5	Benzyl alcohol	10
			Toluene	10
Benzyl alcohol	5	7	Toluene	28
Crotonaldehyde	5	2	*n*-Butyraldehyde	80
			n-Butyl alcohol (trace)	
Acrolein	10	3	Propionaldehyde	93
			n-Propyl alcohol (trace)	
Acrylonitrile	5	<5 min.	Propionitrile	35

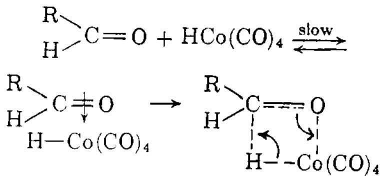
[a] Time to consume 90% of the $HCo(CO)_4$. [b] Based on starting $HCo(CO)_4$, after disappearance of all free $HCo(CO)_4$.

The reduction may be represented by equation (1)

$$RCHO + 2HCo(CO)_4 \longrightarrow RCH_2OH + Co_2(CO)_8 \quad (1)$$

Dicobalt octacarbonyl was isolated from each of the reactions. Some of the octacarbonyl is probably produced by slow decomposition of the hydrocarbonyl as evidenced by the presence of hydrogen in the small quantity of evolved gas. Some of the cobalt remains in solution, probably in the form of an as yet unidentified complex.

A mechanism similar to that proposed by Marko[3] for the high pressure reaction and independently developed by us is suggested as follows



(2)

II

$$II \longrightarrow R{-}CH_2OCo(CO)_4\ (III) \quad (3)$$

$$III + HCo(CO)_4 \xrightarrow{fast} RCH_2OH + Co_2(CO)_8 \quad (4)$$

A semiquantitative kinetic study of these reactions in which the hydrocarbonyl disappearance was measured by a simple titration technique indicates that the reactions are first order with respect to hydrocarbonyl. The hydrocarbonyl appears to function as a hydride donor.

Experimental

All reactions reported in Table I were carried out under one atmosphere of carbon monoxide. Hydrocarbon solutions of hydrocarbonyl were prepared in the usual manner from dicobalt octacarbonyl.[5,6] These solutions were dried by stirring with anhydrous sodium sulfate. The substrate was added neat to the cobalt hydrocarbonyl solution.

The titration of cobalt hydrocarbonyl was carried out in the following manner. Into a 50-ml. Erlenmeyer flask were placed a Teflon covered stirring bar, 10 ml. of water, and several drops of ethanolic phenolphthalein. The flask was covered with a serum stopper and then purged through syringe needles with carbon monoxide. A 1-ml. sample of hexane solution containing hydrocarbonyl was added. The resulting two-phase system was then stirred continuously during titration with 0.01 *N* sodium hydroxide.

When the reaction solutions were cooled in a Dry Ice–acetone bath, crystalline dicobalt octacarbonyl, m.p. 50–51°, was frozen out. The organic reaction products were analyzed quantitatively by vapor phase chromatography.

---

(1) M. Orchin, "Advances in Catalysis," Vol. V, Academic Press, New York, 1953, p. 387.

(2) L. Marko, *Chem. Ind.* (London), 260 (1962).

(3) L. Marko, *Proc. Chem. Soc.*, 67 (1962).

(4) I. Wender, H. W. Sternberg, and M. Orchin, *J. Am. Chem. Soc.*, **75**, 3041 (1953).

(5) M. Orchin and I. Wender, *Anal. Chem.*, **21**, 875 (1949).

(6) L. Kirch and M. Orchin, *J. Am. Chem. Soc.*, **80**, 4428 (1958).

A New Method for the Preparation of Oxamide

EARL H. BROWN, WENDELL D. WILHIDE, AND
KELLY L. ELMORE

Division of Chemical Development, Tennessee Valley Authority, Wilson Dam, Alabama

Received April 16, 1962

Oxamide, $(CONH_2)_2$, was prepared in milligram quantities when Löb[1] exposed formamide vapor to the action of a silent electrical discharge. When the vapor contained water, however, ammonium oxamate and ammonium oxalate were produced instead. From their study of the oxidation by glow-discharge electrolysis of inorganic substrates such as ferrous, azide, ferrocyanide and cerous ions,

---

(1) W. Löb, *Ber.*, **36**, 684 (1913).