Hydrogenations with Cobalt Hydrocarbonyl

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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

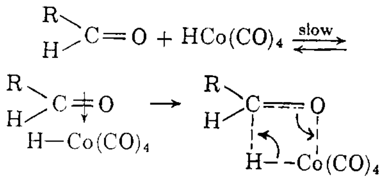
[a] Time to consume 90% of the $HCo(CO)_4$. [b] Based on starting $HCo(CO)_4$, after disappearance of all free $HCo(CO)_4$.

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

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

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

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.

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(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

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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,

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

Denaro and Hickling[2] and Hickling and Linacre[3] reported that the technique yields very high local concentrations of OH radicals in aqueous systems and suggested that it may be useful for electro-organic preparations.

We have converted formamide to oxamide by glow-discharge electrolysis. Most of the runs were made in a two-compartment cell like that described by Hickling, *et al.*[2,3] The discharge between the anode and the solution was maintained by power from a 750-watt fullwave rectifier with a maximum potential of 1500 v.

The electrolyte was usually an 0.8 *N* sulfuric acid solution and the formamide was dissolved in the anolyte. Most runs were made for one hour with 0.06 amp. The potential required for steady operation ranged from 470 to 600 v. The cell was immersed in a stirred ice water bath that maintained the temperature of the anolyte at 12 to 14°. Oxygen was admitted to the top of the anode compartment. Results of three of the better runs are summarized in Table I. The oxamide was a homogeneous, white crystalline product with the correct optical properties and powder X-ray pattern.[4]

Highest yields of oxamide were obtained with a solution of 10 ml. of formamide in 30 ml. of electrolyte in the anode compartment. An acidic electrolyte appeared most satisfactory. High yields were obtained with 0.1 to 0.8 *N* sulfuric acid solutions, but the yields decreased when the concentration of electrolyte was raised to 2 *N*. Increasing the concentration of acid apparently increased the hydrolytic degradation of the formamide. Addition of neutral salts, such as potassium sulfate, to the electrolyte had no significant effect.

Phosphoric acid worked equally as well as sulfuric acid, but a phosphate solution buffered to pH 7 gave low yields, and similar low yields were obtained with 1 *N* sodium hydroxide solution as the electrolyte.

Best operation was obtained when the temperature of the anolyte was above 0 and below 25°. At lower temperatures freezing of the electrolyte, and at higher temperatures excessive volatilization of the anolyte, lowered the yield.

TABLE I

PREPARATION OF OXAMIDE FROM FORMAMIDE BY GLOW-DISCHARGE ELECTROLYSIS

(One-hour runs; O_2 passed through anode compartment; pressure, 30 mm. absolute; catholyte, 40 ml. 0.8 *N* H_2SO_4; anolyte, 10 ml. formamide in 30 ml. 0.8 *N* H_2SO_4)

Current		Oxamide	
Amp.	Volts	Grams	Equivalents/ Faraday[a]
0.06	470	0.2822	2.9
.08	440	.4076	3.1
.12	480	.6073	3.1

[a] To conform to the usual practice of expressing yields in terms of equivalents of product per Faraday, 1 mole of oxamide is assumed to represent 2 equivalents.

The pressure in the cell was maintained at about 30 mm. absolute. High yields of oxamide were obtained when the atmosphere in the cell was oxygen or air, but the yields were low when the atmosphere was carbon monoxide.

Glow-discharge electrolysis of formamide alone also produced oxamide, but at a yield less than 1 equivalent per Faraday and with darkening and considerable decomposition of the formamide.

Ordinary electrolysis of formamide, alone or in an electrolytic solution, yielded no oxamide. In other attempts to prepare oxamide, we found that hydrogen peroxide does not react with formamide alone to yield oxamide. Addition of ferrous sulfate to the system, however, yielded a small amount of oxamide. The Fenton reaction with ferrous sulfate[5] involves the action of free hydroxyl radicals. It thus appears possible that the production of oxamide from formamide by glow-discharge electrolysis also involves free hydroxyl radicals.

(2) A. R. Denaro and A. Hickling, *J. Electrochem. Soc.*, **105**, 265 (1958).

(3) A. Hickling and J. K. Linacre, *J. Chem. Soc.*, 711 (1954).

(4) E. M. Ayerst and J. R. C. Duke, *Acta Cryst.*, **7**, 588 (1954).

(5) J. H. Merz and W. A. Waters, *J. Chem. Soc.*, S15 (1949).

An Effective General Method for Oxidizing Salts of Mononitro Compounds with Neutral Permanganate to Aldehydes and Ketones[1a]

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An important conversion reaction of primary and secondary nitro compounds is the acid-catalyzed hydrolysis of their salts to aldehydes and ketones[2] (the Nef reaction,[3] equation 1), respectively. The conversions have often been accomplished efficiently[3]; if, however, the nitronic acids which are intermediates in the hydrolytic decompositions suffer the consequences of steric factors,[4,5] the yields and the rates of conversion to carbonyl compounds may be greatly minimized. Further disadvantages arise in the Nef reaction if the nitronic acid which is being converted (a) contains other functional groups which are affected by the

$$2R_2C{=}NO_2Na + H_2SO_4 \longrightarrow 2R_2C{=}O + N_2O + Na_2SO_4 + H_2O \quad (1)$$

(1) (a) Abstracted in part from the Ph.D. dissertation of Francis T. Williams, Jr., The Ohio State University, Columbus, Ohio, 1958; (b) Present address: Chemistry Department, Antioch College, Yellow Springs, Ohio.

(2) (a) M. Konovalov, *J. Russ. Phys. Chem. Soc.*, **25**, I. 509 (1893); (b) M. Konovalov, *Ber.*, **29**, 2193 (1896); (c) J. U. Nef, *Ann.*, **280**, 263 (1894).

(3) For a general summary of the Nef reaction, see W. E. Noland, *Chem. Rev.*, **55**, 137 (1955).