

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Reduction of Certain Cobalt Salts in Liquid Ammonia¹

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Data are given to show that, in reaction with potassium in liquid ammonia, cobalt(II) nitrate is converted to cobalt(II) amide, with concomitant reduction of nitrate to nitrite. Cobalt(II) amide and cobalt(III) bromide are reduced principally to elemental cobalt. Data on the comparative activity of this product as a hydrogenation catalyst are included.

The reduction of salts of nickel and iron to the corresponding metals (and other products) by means of liquid ammonia solutions of potassium, and results obtained in the use of these reduction products as catalysts for the hydrogenation of certain olefins have been described in earlier papers from these laboratories.^{2,3} The present paper is concerned with similar data relating to cobalt.

Experimental

With the exceptions noted below, all experimental methods and materials were the same as those described previously.^{2,3}

Cobalt(II) nitrate 6-ammonate was prepared by a minor modification of the method of Ephraim and Rosenberg.⁴ The ammonia content of this salt was found to be extremely sensitive to the temperature employed during its formation.

Anal. Calcd. for $\text{Co}(\text{NO}_3)_2 \cdot 6\text{NH}_3$: Co, 20.7; NH_3 , 35.8. Found: Co, 20.6; NH_3 , 37.0.

Cobalt(III) bromide 6-ammonate was prepared as directed by Bjerrum.⁵

Anal. Calcd. for $\text{CoBr}_2 \cdot 6\text{NH}_3$: Co, 14.7; Br, 59.9. Found: Co, 14.7; Br, 60.0.

Cobalt for use in comparative studies of catalytic activity and related properties was prepared by reducing cobalt(III) oxide with hydrogen⁶ for 22 hr. at 250–260°.

Anal. Found: Co, 100.3.

Reduction of Cobalt(II) Nitrate 6-Ammonate.—In a typical experiment, a solution of 1.345 g. of cobalt(II) nitrate 6-ammonate in 65 ml. of liquid ammonia at -33.5° was titrated with 0.544 *M* potassium solution⁷ until a total of 0.372 g. of the metal had been added [mole ratio $\text{K}/\text{Co}(\text{NO}_3)_2 = 2.02$]. Throughout the course of the reaction a bulky blue precipitate was formed; there was no liberation of hydrogen or other insoluble gas, and the supernatant solution was colorless. The precipitate was washed with liquid ammonia and dried *in vacuo* at room temperature for 3 hr., during which the solid gradually became black. This product was at no time exposed to the atmosphere.

Anal. Calcd. for $\text{Co}(\text{NH}_3)_2$: Co, 64.8. Found: Co, 65.4.

The solid residue remaining after evaporation of the combined filtrate and washings was dissolved in water to form a colorless solution which gave positive tests for nitrite ion (aniline-phenol test) and nitrate ion [brucine-tin(II) chloride test].

Reduction of Cobalt(II) Amide.—Cobalt(II) nitrate 6-ammonate (0.711 g.) was converted to cobalt(II) amide in the manner described above. The amide was washed thoroughly, resuspended in 60 ml. of liquid ammonia and treated with a volume of standard potassium solution approximately 15% in excess of that calculated for reduction of the amide to elemental cobalt. The resulting black solid was washed with ammonia and dried *in vacuo* at room temperature. The resulting solid was found to contain only

90.1% cobalt, and in no case was cobalt(II) amide reduced to a product of higher cobalt content. Largely because of the unattractive physical properties of cobalt(II) amide and the difficulties attendant upon handling this intermediate in the available equipment, neither cobalt(II) nitrate nor cobalt(II) amide was investigated further.

Reduction of Cobalt(III) Bromide 6-Ammonate.—Suspensions of this salt in ca. 65 ml. of liquid ammonia were reduced with potassium added both as solid and in liquid ammonia solution. In either case the bromide was rapidly converted to a black solid, hydrogen was evolved throughout the course of the reaction, and blue-green and red colored solutions were formed depending upon the rate of addition of potassium. Upon completion of the reactions, the insoluble products were washed with ammonia, dried *in vacuo* at room temperature, and at all times protected from the atmosphere since these products were markedly pyrophoric. Solutions of these products in dilute nitric acid did not give positive tests for bromide ion. Representative data that show the effect of variation of reaction ratios and mode of addition of potassium upon the cobalt content of the ammonia-insoluble products are given in Table I, which also includes information relative to different modes of treatment of these products.

TABLE I

REDUCTION OF COBALT(III) BROMIDE WITH POTASSIUM IN LIQUID AMMONIA

Run No.	Salt, g. ^a	K, g.	K/CoBr ₂	Co, % ^b
13	6.789	2.550 ^c	3.85	90.8 ^d
14	3.398	2.749	8.29	92.6 ^e
15	3.422	3.508 ^c	10.5	87.0
16	3.398	2.456	7.41	96.1
18	3.401	2.407	7.26	96.6
19	3.406	2.364	7.12	90.8 ^f
21	3.401	2.156	6.50	93.4 ^g

^a Added in the form of $\text{CoBr}_2 \cdot 6\text{NH}_3$. ^b The cobalt content of fourteen independent reduction products ranged from 86.2 to 96.6%; average, 92.4. ^c Potassium added in liquid ammonia solution. ^d Found: NH_3 , 3.8; K, 3.3; total accounted for, 97.9. ^e Found: NH_3 , 1.1; K, 6.0; total accounted for, 99.7. ^f Ammonia-insoluble product was washed, resuspended in liquid ammonia, and treated with 1.201 g. of ammonium bromide. ^g After washing with ammonia, the insoluble product was removed from the reactor as a slurry in absolute ethanol.

X-Ray Diffraction Patterns.—The presence of elemental cobalt in the products of the reduction of cobalt(III) bromide with potassium in ammonia and of cobalt(III) oxide with hydrogen was established by means of X-ray powder-diffraction patterns using samples mounted in Pyrex capillary tubes. The data are given in Table II; no extraneous lines were observed.

Surface Area Measurements.—By means of a modification⁸ of the method of Bruanauer, Emmett and Teller, the surface area of cobalt from cobalt(III) bromide was found to be 24 m.²/g. Similarly, the area found for cobalt from cobalt(III) oxide was 2 m.²/g. On the basis of electron photomicrographs obtained through the use of an RCA Type EMU-1 electron microscope,⁹ the average particle diameters for cobalt from the oxide and bromide were estimated to be 2.5 and 0.01 micron, respectively. If spherical particles are assumed, the corresponding calculated areas are 1.3×10^{-2} and 8.4 m.²/g., respectively. This marked divergence

(1) This work was supported, in part, by the Office of Naval Research, Contract N6onr-26610.

(2) G. W. Watt, W. F. Roper and S. G. Parker, *THIS JOURNAL*, **73**, 5791 (1951).

(3) G. W. Watt and W. A. Jenkins, Jr., *ibid.*, **73**, 3275 (1951).

(4) F. Ephraim and E. Rosenberg, *Ber.*, **51**, 130 (1918).

(5) J. Bjerrum, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 219.

(6) H. Moissan, *Ann. chim. phys.*, **21**, 242 (1880).

(7) Identical results were obtained in experiments in which the potassium was added as a solid.

(8) H. E. Ries, Jr., R. A. Van Nordstrand and W. E. Kreger, *THIS JOURNAL*, **69**, 35 (1947).

(9) The assistance of L. L. Antes is gratefully acknowledged.

TABLE II
 X-RAY DIFFRACTION DATA FOR COBALT

Co ^a		Co from CoBr ₂ ^b		Co from Co ₃ O ₄ ^c	
<i>d</i>	<i>I</i> / <i>I</i> ₁	<i>d</i>	Relative intensity	<i>d</i>	Relative intensity
2.158	0.25	2.17	Weak	2.15	Weak
2.037	1.0	2.03	Strong	2.02	Strong
1.915	1.0	1.91	Strong	1.90	Strong
1.773	0.15	1.76	Weak	1.79	Weak
1.484	.03	1.50	Weak		
1.250	.5	1.26	Weak	1.25	Weak
1.148	.1	1.14	Weak		
1.066	.6	1.06	Medium	1.06	Medium
1.045	.5			1.04	Weak

^a Data from A.S.T.M. Index of X-Ray Diffraction Patterns. ^b MoK α , Zr filter; 25 hr. exposure at 80 kv. and 20 ma. ^c CuK α , Ni filter; 23 hr. exposure at 80 kv. and 18 ma.

between the measured and estimated values suggests that both cobalt samples were of quite porous structure.

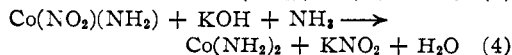
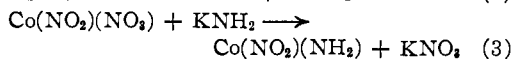
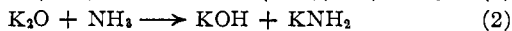
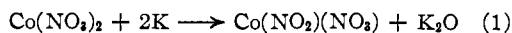
Determination of Adsorbed Hydrogen.—In the manner described previously² samples of the ammonia-insoluble product from the reduction of cobalt(III) bromide were heated at temperatures up to 600° for as much as 17 hr. The hydrogen evolved amounted to an average of 7.1 cc./g. In one case (Table I, Run 19), the hydrogen liberated upon treatment of the ammonia-insoluble product with ammonium bromide in liquid ammonia was measured and found to amount to 6.4 cc./g.

Catalytic Activity.—All evaluations of catalytic activity of cobalt were made using methods and conditions described previously,² with the exception that cobalt catalysts were of the order of 0.2 g. and the duration of pre-treatment with hydrogen was one hour.¹⁰

Although cobalt produced by the reduction of cobalt(III) oxide with hydrogen was found to be entirely inactive as a catalyst for the hydrogenation of allyl alcohol at 30° and 1500 mm. hydrogen pressure, cobalt from the reduction of cobalt(III) bromide in liquid ammonia was active but somewhat less so than Raney nickel. The typical data shown in Fig. 1 illustrate the reproducibility of the catalysis prepared in ammonia (Runs 16 and 18), and the effect of pre-treatment with ammonium bromide (Run 19) and ethanol (Run 21). Rate data for Raney nickel W-6 are included for comparison.

Discussion

The products of the reduction of cobalt(II) nitrate with two atomic equivalents of potassium in liquid ammonia have been shown to consist of insoluble cobalt(II) amide and a mixture of soluble nitrate and nitrite ions. It is difficult to account for these products since hydrogen was not liberated and because potassium hydroxide was not present as an insoluble product at the end of the reactions. The following equations are compatible with the observed facts



The cobalt(II) amide produced in these reactions is identical in physical properties to that produced by Bergstrom¹¹ by the interaction of cobalt(II) thiocyanate and potassium amide in liquid ammonia. The reduction of nitrate to nitrite by solu-

(10) The pre-treatment was extended from 15 min. to 1 hr. to eliminate an induction period more pronounced in the case of cobalt than previously observed in studies involving nickel.³

(11) F. W. Bergstrom, *THIS JOURNAL*, **46**, 2631 (1924).

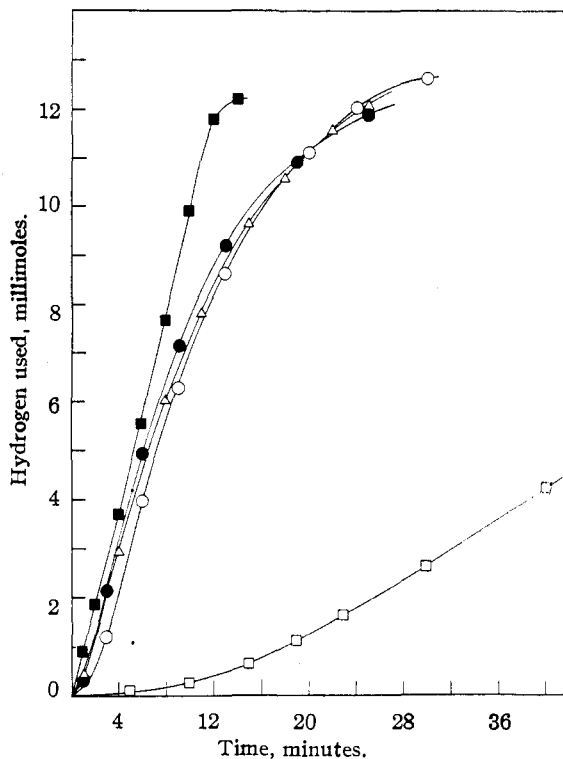
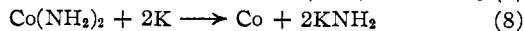
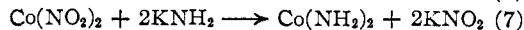
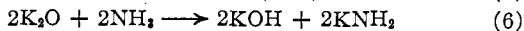
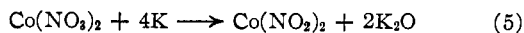


Fig. 1.—Hydrogenation of allyl alcohol over cobalt catalysts: O, Co, 0.196 g., run no. 16; ●, Co, 0.203 g., run no. 18; □, Co, 0.139 g., run no. 19; Δ, Co, 0.205 g., run no. 21; ■, Raney Ni, 0.0206 g.

tions of metals in ammonia has been observed previously,^{12,13} and equation (2) represents a well known reaction.¹⁴

When, in an effort to reduce the cobalt(II) amide to elemental cobalt, excess potassium (as much as seven atomic equivalents) is added, substantially all of the nitrate ion is reduced to nitrite, and the ammonia-insoluble product consists principally of potassium hydroxide and elemental cobalt together with small quantities of impurities containing cobalt, nitrogen and potassium. Variable quantities of hydrogen are liberated (owing to conversion of excess potassium to potassium amide under the catalytic influence of the elemental cobalt). These products may be accounted for by reactions occurring subsequent to those represented by equations (1) to (4) or by the equations



Except for the formation of small quantities of by-products containing potassium and nitrogen, the reduction of cobalt(III) bromide with potassium produces principally elemental cobalt. In contrast to cobalt formed by reduction of cobalt(III) oxide with hydrogen, the product from the bromide exhibits marked activity as a catalyst for the hydrogenation of allyl alcohol at room tem-

(12) W. M. Burgess and F. R. Holden, *ibid.*, **59**, 461 (1937).

(13) F. W. Bergstrom, *ibid.*, **62**, 2381 (1940).

(14) C. A. Kraus and E. F. Whyte, *ibid.*, **48**, 1781 (1926).

perature and a hydrogen pressure of two atmospheres. The catalytic activity is quite reproducible despite considerable variation in the cobalt content of the ammonia-insoluble product. These catalysts are largely deactivated by treatment with ammonium bromide (an acid) in liquid ammonia and it is of interest to note that the quantity of hydrogen thereby liberated is in good agreement with that obtained by thermal desorption. These catalysts are also somewhat deactivated by *extensive* washing with, or long periods of storage under,

absolute ethanol, although as shown in Fig. 1 (Run 21) their activity is substantially uninfluenced by limited exposure to ethanol. Preliminary studies of the kinetics of the hydrogenation reaction indicate that it is first order with respect to the concentration of allyl alcohol. The significance of this fact, as well as the surface area data, will be considered in later papers concerned with other transitional metal catalysts formed by the reduction of salts in liquid ammonia.

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The Thermal Dissociation of Some Chromium(III) Iodides

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Equilibrium pressures of iodine above CrI_3 , CrICl_2 and CrIBr_2 have been measured. Thermodynamic properties of the last two are similar to those anticipated for a solid solution of CrI_3 and CrX_3 , as suggested by structural properties. However, no definite conclusion has been drawn concerning the character of the mixed halide phases.

The structural characteristics of CrICl_2 and CrIBr_2 (prepared by reaction of iodine with CrCl_2 and CrBr_2 , respectively) are similar to those which would be anticipated for a solid solution of the parent compounds CrI_3 and CrX_3 .¹ In view of the reversible nature of the reaction between iodine and the chromium(II) halides, it was considered of interest to investigate the thermodynamic properties of the mixed halide phases by a study of the thermal decomposition equilibria. The data obtained are compared with results previously reported for CrI_3 ² and CrCl_3 .^{3,4} The thermal dissociation of CrI_3 has been reinvestigated by a different method which is found to give the thermodynamic constants confirming earlier results within experimental error.

Experimental

Preparation and identification of the materials have been discussed previously.^{1,2} Two methods were used to measure iodine pressures: the Knudsen effusion technique,^{5,2} and a static method of employing a thin Pyrex glass diaphragm gage.^{6,7} A comparison of results from the two methods (by extrapolation) suggests that a rate problem is encountered in the effusion apparatus (*i.e.*, the sample is unable to maintain the equilibrium pressure with pinhole diameters of the order of 1 mm.) which leads to apparent equilibrium pressures (steady state pressures) lower than the true values. In the case of CrI_3 the results were not sufficiently different to affect thermodynamic quantities appreciably beyond experimental error. This was not true for the mixed halides, however. Diaphragm gage pressures were used exclusively for the data reported in this paper.

The manometer described previously⁷ was modified slightly for experiments with CrI_3 and CrIBr_2 . Some of the temperatures at which measurements were made for these two compounds were above the softening point of Pyrex. Hence a quartz bottom was attached to the apparatus and the temperature of the sample maintained at higher values than the diaphragm. For the majority of runs, the dia-

phragm was held at 200°. The pressure has been assumed constant within experimental uncertainty (± 2 mm.) throughout the apparatus (although there will obviously be continuous circulation). The validity of this assumption was substantiated by variation of the temperature of the diaphragm portion of the system while the sample temperature was held constant. The equilibrium pressure was not observed to change. The CrICl_2 system was studied with the entire apparatus at a uniform temperature.

Equilibrium pressures were also verified by an isopiestic method. With the sample at a given temperature, the pressure of iodine was determined by measuring the temperature of a cool portion of the tube (in a thermostat) at the point where iodine crystals began to grow, and conversely the temperature at which iodine crystals at this point evaporate. This method was not capable of great precision but taken with known vapor pressures of iodine gave results compatible with those obtained with the diaphragm gage.

Data for all compounds were checked with several independently prepared samples, including one series in each case where the material was formed in the apparatus by direct reaction of iodine with the chromium(II) salt. The relative amounts of chromium(III) and chromium(II) phases were also varied without significant effects on the equilibrium constant for the decomposition. These results indicate that the chromium(III) mixed halide phases maintain an essentially constant composition throughout the decomposition and hence behave effectively as a single component in so far as the phase rule is concerned.

It has been assumed that iodine is the only component present at significant concentrations in the gas phase. Appreciable amounts of chlorine or bromine would not be anticipated from thermodynamic considerations, and this view is supported by the nature of the thermal decomposition products. Doerner⁸ finds the chloride system to be complicated at high temperatures by the presence of CrCl_4 in the vapor phase. However, the concentration of this substance is not significant at 400°, the highest temperature involved in the study of the CrICl_2 system. One would expect CrBr_4 and CrI_4 to be considerably less stable than CrCl_4 and have assumed neither to be present in significant amounts in the bromide or iodide systems. Absence of volatile compounds of chromium is also indicated by the lack of transport of chromium from the hot regions by sublimation.

Results and Discussion

The data for the three iodides are shown graphically in Fig. 1. The experimental points are given and the lines drawn correspond to the equations below as determined by a least squares fit of the data.

- (1) L. L. Handy and N. W. Gregory, *THIS JOURNAL*, **74**, 891 (1952).
- (2) L. L. Handy and N. W. Gregory, *ibid.*, **72**, 5049 (1950).
- (3) H. A. Doerner, *Bur. Mines T. P.*, **577**, U. S. Govt. Pt. Off. (1937).
- (4) C. G. Maier, *Bur. Mines Bull.*, **436**, U. S. Govt. Pt. Off. (1942).
- (5) M. Knudsen, *Ann. Physik*, **28**, 1002 (1909).
- (6) F. Daniels, *THIS JOURNAL*, **50**, 1115 (1928).
- (7) N. W. Gregory and B. A. Thackrey, *ibid.*, **72**, 3176 (1950).