

tion of the absorption curve with the temperature is not sufficient to affect the values of ΔH by more than about 1 kcal. Accordingly, it seems very unlikely that the theory of Pauling and Wheland can be applied without modification to the calculation of heats of dissociation of hexaarylethanes in solution.

Summary

1. The heat of dissociation of di- β -naphthyl-tetraphenylethane and minimum values for the

heats of dissociation of three other hexaarylethanes have been calculated from data available in the literature.

2. The results indicate that the entropy of dissociation of hexaarylethanes is not entirely independent of the nature of the aryl groups.

3. The heat of dissociation of di- β -naphthyl-tetraphenylethane in solution does not agree with the value calculated on the basis of Pauling and Wheland's resonance theory.

PROVIDENCE, R. I.

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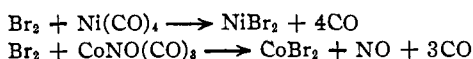
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 55]

Preparation and Properties of Cobalt Nitrosyl Carbonyl and of Cobalt Carbonyl Hydride

BY GEORGE W. COLEMAN AND ARTHUR A. BLANCHARD

Blanchard and Windsor¹ in summarizing the properties of the volatile carbonyls, nitrosyl carbonyls and carbonyl hydrides of the metals, noted that in the volatile $\text{CoNO}(\text{CO})_3$ the total of the atomic numbers is the same as in the volatile $\text{Ni}(\text{CO})_4$; also that in the suspected volatile $\text{HCo}(\text{CO})_4$ the same total of atomic numbers prevails.

In order to add further evidence of the similarity of the structure of $\text{Ni}(\text{CO})_4$ and $\text{CoNO}(\text{CO})_3$ the present study was undertaken to determine whether the action of bromine would liberate nitric oxide as well as carbon monoxide



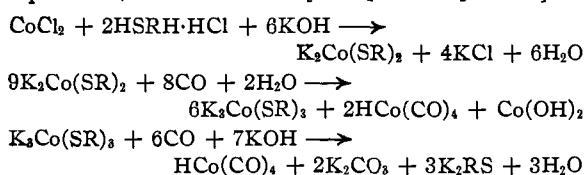
Complete proof has been found that bromine does, in fact, give the expected reaction.

Incidentally, in preparing an additional supply of cobalt nitrosyl carbonyl, a greatly improved procedure has been worked out through adapting methods employed by Schubert² in studying the action of carbon monoxide with cysteine complexes of cobalt.

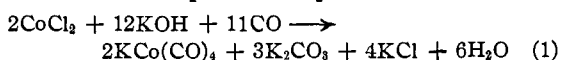
Also in the course of this procedure it has been possible to isolate the volatile hydride of cobalt carbonyl, $\text{HCo}(\text{CO})_4$, in pure form and contribute to a knowledge of its properties.

Windsor and Blanchard³ and Blanchard, Rafter and Adams⁴ studied the formation of carbonyls

when alkaline suspensions of nickel and cobalt sulfides and cyanides are treated with carbon monoxide. They did not attempt to identify intermediate complexes. Schubert, using cysteine compounds instead of sulfides or cyanides, isolated the intermediate stages, and defined the course of the reaction with cobalt salt with the equations, in which $\text{R} = [-\text{CH}_2\text{CHNH}_2\text{COO}-]$:



The present authors would make a summation of the above steps in the equation



which shows a complete regeneration of the cysteine, a reduction of cobalt and a corresponding oxidation of carbon monoxide.

Schubert acidified the alkaline solution containing the complex $\text{KCo}(\text{CO})_4$, and noted that a very bad odor was produced and that crystals separated which he identified as the dimeric cobalt tetracarbonyl $\text{Co}_2(\text{CO})_8$. He was unable to detect either free hydrogen or any product to account for the hydrogen liberated from the postulated hydride $\text{HCo}(\text{CO})_4$.

Experimental

Auxiliary Substances Promoting Absorption of Carbon Monoxide.—Several auxiliary substances other than

(1) Blanchard and Windsor, *THIS JOURNAL*, **56**, 826 (1934).

(2) Schubert, *ibid.*, **55**, 4563 (1933).

(3) Windsor and Blanchard, *ibid.*, **55**, 1877 (1933).

(4) Blanchard, Rafter and Adams, *ibid.*, **56**, 16 (1934).

cyanides, sulfides and cysteine were tried, and the rate of absorption of carbon monoxide by an alkaline solution or suspension of cobaltous salt in the shaking apparatus⁵ was measured. The results are shown in the tabulation. The shaking apparatus was filled with carbon monoxide, concentrated solutions of the various ingredients were run in, the volume was made up to 80 cc. and shaking was started with the cock open from the carbon monoxide reservoir. Concentrations are given in f. w. of the added substance per liter of the final volume of the mixture.

Cyanide, tartrate and cysteine produced the most notable absorption. Following the absorption of carbon monoxide, treatment of the alkaline cyanide solution with nitric oxide immediately produced brown vapors of cobalt nitrosyl carbonyl as already noted by Rafter and Adams, but similar treatment of the tartrate and cysteine solutions with nitric oxide was without effect.

Acidification of the cysteine solution following treatment with carbon monoxide and nitric oxide produced brown vapors which, when swept with carbon monoxide and nitric oxide through a tube filled with phosphorus pentoxide, and through a trap immersed in solid carbon dioxide and alcohol, condensed in the latter to a yellow solid which melted to a deep red liquid. When this liquid came to room temperature it very quickly changed to a dark colored crystalline mush. In this run the vapors blackened the connecting tubes and the phosphorus pentoxide tube through which they passed on the way to the trap. In the runs described later this blackening did not occur. Later experiments confirmed the conjecture that the dark red vapors contained both $\text{Co}(\text{CO})_2\text{NO}$ and $\text{HCo}(\text{CO})_4$.

$\text{Co}(\text{NO})_2$	Auxiliary substance and concentration		KOH	Absorption of CO
0.5	$\text{K}_2\text{C}_2\text{O}_4$	2.0	6	None in 1 hour
.25	$\text{K}_2\text{C}_2\text{O}_4$	1.0	3	None in 2.5 hours
.5	$\text{H}_2\text{C}_4\text{H}_6\text{O}_6$	2.0	6	5 cc. in 1 hour
.5	$\text{H}_2\text{C}_4\text{H}_6\text{O}_6$	2.0	24	147 cc. in 5.25 hours
.5	$\text{H}_2\text{C}_4\text{H}_6\text{O}_6$	2.0	16	1700 cc. in 144 hours
.5	$\text{CH}_2\text{NH}_2\text{COOH}$	2.0	6	None in 0.5 hour
.5	$\text{CH}_2\text{NH}_2\text{COOH}$	2.0	12	3 cc. in 0.5 hour
.5	$\text{CH}_2\text{NH}_2\text{COOH}$	2.0	24	20 cc. in 2 hours
.5	$\text{CH}_2\text{NH}_2\text{COOH}$	2.0	3	10 cc. in 0.5 hour
.1	$\text{CH}_2\text{NH}_2\text{COOH}$	0.4	6	5 cc. in 0.5 hour
.5	CH_3CHNH_2	2.0	6	None in 0.5 hour
.5	KCNS	0.5	6	15 cc. in 2.5 hours
.5	$\text{C}_6\text{H}_4(\text{OH})_2$	2.0	6	10 cc. in 2 hours
.5	KCN	0.5	2	355 cc. in 1.25 hours
.5	H_3BO_3	0.5	2	None in 1 hour
.5	$\text{C}_6\text{H}_5\text{COONa}$	2.0	6	5 cc. in 2 hours
.5	$\text{HOOC}\cdot\text{CH}_2\text{CH}_2\cdot\text{CHNH}_2$ COOH	2.0	6	None in 2 hours
.5	$\text{HSCH}_2\text{CHNH}_2\text{COOH}\cdot\text{HCl}$	0.75	16	5465 cc. in 149 hours

Preparation of Cobalt Nitrosyl Carbonyl

First Run.—Sixty cc. of a solution 0.5 formal in cobalt nitrate, 0.75 formal in cysteine hydrochloride and 16 formal in potassium hydroxide absorbed carbon monoxide in the shaker at the rate of 160 cc. per hour at the start and the rate had diminished to 5 cc. per hour at the end of one hundred and forty-nine hours. In all, 5500 cc. of carbon monoxide was absorbed (4100 calculated according to

equation (1)). One half of this solution was run into another tube for a later experiment (air being at all times excluded), and the half left in the shaking apparatus was treated with concentrated hydrochloric acid. Violent local effervescence took place at first, the carbon dioxide redissolving in the rest of the solution on shaking. Finally, the gas came off violently and one-half of the solution was lost by being blown out of the apparatus. The odor was so noxious that work had to be suspended until the laboratory was thoroughly ventilated.

After a slight excess of acid had been added to the one-half of the solution that was saved, the color was yellow and a black scum floated on top. Not more than a trace of solid had been collected in the trap during the acidification. A new trap was now introduced, and nitric oxide was run into the shaking apparatus which immediately became filled with reddish-brown vapors. The vapor was swept with nitric oxide through a phosphorus pentoxide tube into the trap cooled with dry ice, where a yellow solid collected. Thirty minutes later more reddish-brown vapors had collected which were again swept into the trap. The reddish-brown vapors continued to form for several days and were occasionally swept into the trap. In all 0.7 g. of yellow solid, melting sharply at approximately -11° to a deep red liquid, was collected. Thus a yield of $\text{Co}(\text{NO})(\text{CO})_2$ of about 54% based on the cobalt nitrate taken, was obtained.

Preparation of Cobalt Carbonyl Hydride

First Run.—The one-half of the solution reserved in the first part of the first run as above described was again in-

troduced into the shaking apparatus without coming in contact with air. The train of phosphorus pentoxide tube and trap cooled with dry ice was again attached. Concentrated hydrochloric acid was added, this time with very great caution until an additional 1 cc. produced no more effervescence. After five minutes of shaking, a very pale yellow gas was noted, and this, swept with carbon monoxide into the trap, condensed to a pale yellow solid. Addition of more acid gave rise to more yellow gas. In all 11 cc. of normal hydrochloric acid was used before the yellow

(5) Rafter, Thesis, Massachusetts Institute of Technology, 1932.

gas ceased to be produced (thus making the solution about 1 normal in free hydrochloric acid). The remaining solution was yellow with some black scum ($\text{Co}_2[\text{CO}]$) floating on top. The yellow solid collected in the trap melted sharply at -33° to a sulfur yellow liquid; after it was resolidified it was yellow; it became somewhat reddish after a few remeltings. At room temperature it showed effervescence and soon changed to a brown solid. This solid was then heated to 51° at which temperature it melted. Of the total gas evolved up to 51° a sample of 24.8 cc. was collected. Of this 10.3 cc. was absorbed by ammoniacal cuprous chloride, thus indicating 41.6% of carbon monoxide, and explosion with oxygen indicated 48.8% of hydrogen. The gas evolved on thus warming the hydride had a pale yellow color. Surrounding the upper part of the eudiometer with a cooling bath a thin deposit of yellow solid appeared at -23° and the remaining gas was colorless. This solid had completely reevaporated when the bath temperature reached -11° . The volume decrease, due to the lowering of temperature of the upper one quarter of the gas tube and the condensation of the yellow constituent, was only 0.8 cc. Heating the tube to 250° caused no deposition of a cobalt mirror. This yellow constituent of the gas was not absorbed by concentrated potassium hydroxide nor by ferrous sulfate solution but it was removed by ammoniacal cuprous chloride solution.

The brown residue left after warming the hydride weighed 0.6605 g. It melted again at 51° and gave off gas freely at 60° ; after it was heated to 250° , a brilliant black mirror covered the inside of the entire heated part of the tube; weight of mirror 0.2408 g. Calcd. for Co in $\text{Co}_2(\text{CO})_8$, 0.2275. Volume of gas (all absorbed by ammoniacal CuCl) 385.5 cc. Calcd. for CO, 371 cc. Yield of $\text{HCo}(\text{CO})_4 = 26\%$ based on $\text{Co}(\text{NO})_2$ taken.

Second Run.—Fifty cc. of a solution 0.5 formal in cobalt nitrate; 0.3 formal in cysteine hydrochloride and 16 formal in potassium hydroxide absorbed a total of 4445 cc. of carbon monoxide [3400 calculated according to equation (1)]. Adding 12 normal hydrochloric acid until the solution was acid caused only a slight deposition of the hydride in the trap. On adding 20 cc. excess of 12 *N* hydrochloric acid and sweeping with carbon monoxide a yield of 0.4215 g. of the hydride was collected in the trap (10% yield). Again only a part of the gas from the decomposition of the hydride was collected and this proved to contain 50% hydrogen, and 50% carbon monoxide. This gas also contained the same yellow constituent as in the first run.

Third Run.—Fifty cc. of a solution 0.5 formal in cobalt nitrate; 2.0 formal in tartaric acid and 16 formal in potassium hydroxide absorbed 1700 cc. of carbon monoxide in one hundred and forty-four hours. The solution was a clear cherry red. Strong acidification and sweeping with carbon monoxide gave 0.2074 g. of the hydride or a 10% yield. The remaining solution was pink. The melting point and the odor of the hydride were identical with those of the product obtained in the first and second runs with cysteine. On letting the trap warm up to room temperature, 18.4 cc. of a light yellow gas was obtained. The light yellow constituent again condensed to a solid at -11° . Analysis gave 3.4 cc. of carbon monoxide and 12.8 cc. of hydrogen; calculated for 0.2074 g. of $\text{HCo}(\text{CO})_4 = 14.9$ cc. H_2 .

Treatment of Cobalt Nitrosyl Carbonyl with Bromine

Experiment 1.—0.0208 gram of $\text{Co}(\text{NO})(\text{CO})_8$, prepared by Adams by the cyanide method = 0.000122 f. w., dissolved in 5 cc. of carbon tetrachloride. Add 0.0750 g. $\text{Br}_2 = 0.00041$ f. w., dissolved in 15 cc. of carbon tetrachloride. Effervescence was noted. Found, 2.6 cc. NO; calculated for $\text{Co}(\text{NO})(\text{CO})_8$, 2.9 cc. Found 8.7 cc. CO; calcd., 8.7 cc.

Experiment 2.—0.0624 gram of $\text{Co}(\text{NO})(\text{CO})_8$, prepared by Adams by the cyanide method = 0.000361 f. w., dissolved in 15 cc. of CCl_4 . Add 0.225 g. $\text{Br}_2 = 0.0015$ f. w. dissolved in 15 cc. of CCl_4 . Found, 8.4 cc. NO; calcd. 8.7 cc. Found, 25.9 cc. CO; calcd. 26.2 cc.

Experiment 3.—0.2129 gram of $\text{Co}(\text{NO})(\text{CO})_8$, prepared by the cysteine method in first run above = 0.00123 f. w., dissolved in 15 cc. of CCl_4 . Titrated with a solution of Br_2 in CCl_4 containing 0.01855 g. of Br_2 per cc. The end-point is the disappearance of the red color of the nitrosyl carbonyl followed by the appearance of the red color of bromine. It is difficult to observe because of the green precipitate of anhydrous CoBr_2 . End-point at 10.65 cc. = 0.00123 f. w. Br_2 ; added 1 cc. more Br_2 . Found, 26.0 cc. NO; calcd., 29.5 cc. Found, 88.4 cc. CO; calcd. 88.7 cc. Found, 0.260 g. CoBr_2 ; calcd., 0.268 g.

Experiment 4.—0.2163 gram = 0.00125 f. w. of $\text{Co}(\text{NO})(\text{CO})_8$, dissolved in 15 cc. of CCl_4 . Add 0.2022 g. of Br_2 , dissolved in 10.9 cc. of $\text{CCl}_4 = 0.00126$ f. w., which just gave end-point. Found, 29.9 cc. NO; calcd. 30.1 cc. Found, 89.3 cc. CO, calcd., 90.3 cc. Found, 0.2743 g. CoBr_2 ; calcd., 0.2735 g.

The above experiments show that nitric oxide and carbon monoxide are dislodged quantitatively by bromine both when the exact amount and when an excess of the latter is used. The same results were obtained with samples of cobalt nitrosyl carbonyl prepared by different methods.

Comments

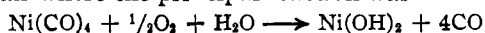
The small amount of yellow gas admixed with the hydrogen obtained on warming $\text{HCo}(\text{CO})_4$ to room temperature is very perplexing. Its melting point at above -23° is too high for it to be some undecomposed hydride. Since it does not give a cobalt mirror even at 250° , it is unlikely that it contains cobalt. One might surmise that it came from some side reaction of the cysteine, were it not for the fact that it is also obtained when tartaric acid instead of cysteine is used as the auxiliary substance. Its amount is small and its presence does not invalidate the main conclusion as to the formation of the volatile hydride and the decomposition of the latter into hydrogen and dimeric cobalt tetracarbonyl. Nevertheless its nature should be studied as soon as opportunity offers.

It appears that cobalt carbonyl hydride is a somewhat stronger acid than carbonic acid, for it is hardly displaced from its salt at all by carbonic acid, and it is not wholly driven from the solution

until free hydrochloric acid in 1 *N* concentration is present.

The net result of the use of tartaric acid appears to be the same as that from the use of cysteine and can be represented by the same equation (1). Probably intermediate complexes of a similar nature are formed.

The metering of the carbon monoxide was only approximate. In the first and second runs the excess of CO absorbed over that required by equation (1) is real, it is doubtless due to the formation of some potassium formate. Blanchard and Gilliland⁶ noted the formation of a little nickel formate in the slow oxidation of nickel carbonyl by air where the principal reaction was



Summary

Bromine reacts quantitatively with cobalt nitrosyl carbonyl, displacing nitric oxide and carbon monoxide.

(6) Blanchard and Gilliland, *THIS JOURNAL*, **45**, 872 (1926).

The absorption of carbon monoxide by alkaline cobalt salt solutions is promoted by the presence of cysteine, tartrate and several amino acids as well as the presence of cyanide and sulfide.

Acidification of the KCo(CO)_4 solution obtained by treating alkaline cobalt salt solution containing cysteine or tartrate with carbon monoxide sets free the very volatile hydride HCo(CO)_4 . This hydride can be condensed to a light yellow crystalline solid which melts at -33° to a sulfur yellow liquid and decomposes at room temperature into the non-volatile dimeric cobalt tetracarbonyl and hydrogen. The hydride is distinctly an acid, its acid strength being markedly greater than that of carbonic acid.

Cobalt nitrosyl carbonyl is most advantageously prepared by the use of cysteine as above: after acidification, the hydride is allowed to decompose in the shaking apparatus, then treatment with nitric oxide yields the nitrosyl carbonyl.

CAMBRIDGE, MASS.

RECEIVED JULY 28, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Action of Bromine in Methyl Alcoholic Solution on Phenanthrene; a New Route to 9-Phenanthrol and 9-Phenanthrylamines¹

BY L. F. FIESER, R. P. JACOBSEN² AND C. C. PRICE

In connection with a study of the reaction between phenanthrene and bromine in carbon tetrachloride solution,³ a trial was made of the action on the hydrocarbon of a solution of bromine in methyl alcohol. Considering the ready formation of phenanthrene dibromide, and in analogy with known cases of the addition of methyl hypobromite to aliphatic and alicyclic ethylenic linkages,⁴ it seemed possible that the hydrocarbon might add the reagent in a similar fashion.

In the first experiments fine, colorless needles of a reaction product were observed to separate after mixing methyl alcoholic solutions of bromine and phenanthrene at room temperature, but the

(1) The bromination reaction described in this paper was discovered in the course of other work by C. C. Price, who made a preliminary study of the formation of the product and of its conversion to 9-methoxyphenanthrene (Dissertation, 1936). A more detailed investigation of the formation, nature and preparative uses of the compound was subsequently made by R. P. Jacobsen, and these experiments form the basis of the present report.—L. F. F.

(2) Du Pont Research Fellow.

(3) Price, *THIS JOURNAL*, **58**, 1834 (1936).

(4) Conant and Jackson, *ibid.*, **46**, 1727 (1924); Jackson, *ibid.*, **48**, 2166 (1926); Jackson and Pasiut, *ibid.*, **49**, 2071 (1927); Meinel, *Ann.*, **510**, 129 (1934).

yield was poor. The results were somewhat improved by working at a lower temperature and by using a large excess of bromine, and it was found that the yield is increased very substantially by carrying out the reaction in the presence of sodium acetate to displace the bromine equilibrium in favor of the hypobromite. Eventually an easily reproducible procedure was developed by means of which a colorless product can be obtained in a quantity amounting to about one and one-third the weight of hydrocarbon employed. This material was granular and possibly different from that first observed. Purified by careful recrystallization, the substance melted at $107.5\text{--}108^\circ$, dec., and when stored in the cold room (5°) it remained apparently unaltered for about one day. At room temperature decomposition set in after a few hours. Although the analysis of the unstable substance presented difficulties, the results for carbon, hydrogen, bromine and methoxyl all point to the formula of a molecular compound composed of equivalent parts of phenanthrene