in 2 ml. of 2-propanol deposited 0.67 g. of colorless solid after standing at 25° for 2 days. The supernatant deposited a further 0.35 g. of solid following the addition of 3 drops of piperidine and long standing. The solid crystallized from acetic acid as very fine colorless needles, m.p. 204–205°.

Anal. Calcd. for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71; mol. wt., 330. Found: C, 68.92; H, 6.89; mol. wt. (Rast procedure in tribromophenol), 370 ± 50.

The structure of this product was not established, but it appears, according to analysis and molecular weight, to be constituted from two molecules of 1,2-cyclohexanedione and one of benzaldehyde. The infrared absorption spectrum, determined on a Nujol mull, exhibited maxima at 1654 (conjugated C=O), 1629 (conjugated C=C), and at 3470, 3369 and 3327 cm.$^{-1}$ (all O–H). The product was insoluble in most organic solvents, appeared to add bromine reversibly, and was rapidly oxidized by potassium permanganate in acetone. Attempts to dehydrate the compound by iodine treatment were unsuccessful. We prefer not to suggest a structure for this substance at the present time of writing since several formulations are still possible with the information on hand.

4,4-Dimethyl-1,2-cyclohexanedionedioxime.—This compound was obtained from 4,4-dimethylcyclohexanone[19] by selenium dioxide oxidation followed by oximation,[20] colorless microcrystals from water, m.p. 162–170°.

Anal. Calcd. for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.50; H, 8.62; N, 16.29.

1,2-Cycloöctadecanedione-bis-2,4-dinitrophenylhydrazone.—Treatment of 2-hydroxycycloöctadecanone[21] with 2,4-dinitrophenylhydrazine in the usual manner formed the osazone, orange needles from methyl ethyl ketone, m.p. 231–232°.

Anal. Calcd. for $C_{30}H_{40}N_8O_8$: C, 56.24; H, 6.29; N, 17.49. Found: C, 56.50; H, 6.36; N, 17.52.

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(19) R. F. Miller and R. Adams, THIS JOURNAL, **58**, 787 (1936).

(20) C. C. Hack, C. V. Banks and H. Diehl, *Org. Syntheses*, **32**, 35 (1952).

(21) M. Stoll and J. Hulstkamp, *Helv. Chim. Acta*, **30**, 1815 (1947).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE U. S. DEPARTMENT OF THE INTERIOR, BUREAU OF MINES, SYNTHETIC FUELS RESEARCH BRANCH]

The Chemistry of Metal Carbonyls. II. Preparation and Properties of Cobalt Hydrocarbonyl[1]

BY HEINZ W. STERNBERG, IRVING WENDER, ROBERT A. FRIEDEL AND MILTON ORCHIN

RECEIVED DECEMBER 6, 1952

A rapid and simple method is described for preparing cobalt hydrocarbonyl from dicobalt octacarbonyl. Kinetic data indicate that the decomposition of cobalt hydrocarbonyl is a second-order reaction, and that k is approximately 3×10^{-3} (mole/liter)$^{-1}$ second^{-1}. In aqueous solution cobalt hydrocarbonyl is stable, completely dissociated, and sparingly soluble. Infrared spectra of cobalt hydrocarbonyl, cobalt deuterocarbonyl and dicobalt octacarbonyl are presented. No –OH band could be detected in the infrared spectrum of cobalt hydrocarbonyl at the concentrations studied.

Although cobalt hydrocarbonyl was first isolated[2] in 1936, comparatively little is known concerning its properties. The development in this Laboratory of a convenient method of preparation provided an opportunity to study some of the properties of this unusual compound.

Preparation of Cobalt Hydrocarbonyl.—Dicobalt octacarbonyl, on treatment with pyridine,[1] disproportionates according to equation (1)

$$12C_5H_5N + 3[Co(CO)_4]_2 \longrightarrow 2[Co(C_5H_5N)_6]^{++}[Co(CO)_4]_2^- + 8CO \qquad (1)$$

It has now been found that dropwise addition to excess dilute sulfuric acid of the pyridine solution containing the salt produces the free hydrocarbonyl, which can be swept out of the reaction mixture in a current of carbon monoxide. Condensation after passage through a phosphorus pentoxide drying tube gives pure hydrocarbonyl in a yield of 95%.[3]

Stability of Cobalt Hydrocarbonyl.—Although cobalt hydrocarbonyl decomposes[5] rapidly as a liquid above its melting point (–26°) according to equation (2a)

$$2HCo(CO)_4 \longrightarrow H_2 + [Co(CO)_4]_2 \qquad (2a)$$

$$2[Co(CO)_4]_2 \rightleftarrows [Co(CO)_3]_4 + 4CO \qquad (2b)$$

it is fairly stable in the gas phase. Hieber[5] studied the decomposition in a closed vessel and emphasized that the last traces of cobalt hydrocarbonyl decomposed very slowly. Also it has been previously reported and amply verified that cobalt hydrocarbonyl can be carried through an absorption train in a current of carbon monoxide[4] without noticeable decomposition. These facts implied and previous workers have assumed[6] that the presence of hydrogen and/or carbon monoxide somehow stabilized the hydrocarbonyl. While carbon monoxide stabilizes dicobalt octacarbonyl (equation 2b) it can effect a stabilization of the hydrocarbonyl only if equation (2a) is reversible. If indeed this were the case, it would be necessary for the reverse reaction of equation (2a) to occur at a finite rate. Experimental data bearing on this point were secured as follows: To a gas mixture containing equimolar (volume) quantities of hydrogen, deuterium and carbon monoxide at room temperature was added 1 volume per cent. of gaseous cobalt hydrocarbonyl. If equation (2a) were reversed under these conditions, the formation of some deuterocarbonyl would be expected according to equation (3)

$$D_2 + [Co(CO)_4]_2 \longrightarrow 2DCo(CO)_4 \qquad (3)$$

The decomposition of the deuterocarbonyl on collision with the hydrocarbonyl should provide HD according to equation (4)

$$HCo(CO)_4 + DCo(CO)_4 \longrightarrow HD + [Co(CO)_4]_2 \qquad (4)$$

The gas mixture was allowed to stand four days at

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[1] I. Wender, H. W. Sternberg and M. Orchin, THIS JOURNAL, **74**, 1216 (1952); paper I in this series.

[2] G. W. Coleman and A. A. Blanchard, *ibid.*, **58**, 2160 (1936).

[3] If dicobalt octacarbonyl is available this method of preparation of cobalt hydrocarbonyl is to be preferred to previous methods.[4,5]

[4] A. A. Blanchard and P. Gilmont, THIS JOURNAL, **62**, 1192 (1940).

[5] W. Hieber and H. Schulten, *Z. anorg. allgem. Chem.*, **232**, 29 (1937).

[6] P. Gilmont and A. A. Blanchard, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 242.

room temperature and then analyzed in the mass spectrometer. No HD could be detected. Obviously, the hydrocarbonyl is not stabilized at room temperature and atmospheric pressure by either carbon monoxide or hydrogen, and equation (2a) is not an equilibrium reaction under these conditions.

A plausible explanation for the relative stability of cobalt hydrocarbonyl in the gas phase is the assumption that the decomposition of cobalt hydrocarbonyl (equation 2a) is a second-order reaction. The rate of decomposition of cobalt hydrocarbonyl then should be proportional to the square of its concentration (equation 5)

$$-\mathrm{d}\ \mathrm{HCo(CO)_4}/\mathrm{d}t = k[\mathrm{HCo(CO)_4}]^2 \qquad (5)$$

This assumption was substantiated by a kinetic study. An evacuated gas cell was filled with gaseous cobalt hydrocarbonyl, and the rate of its decomposition at 25 ± 0.2° was determined by measuring the change in absorbance value (A) with time of an infrared absorption band at 5.01 μ. During 4475 minutes, 8 measurements were made; the absorbance value decreased from 0.686 to a final value of 0.150. Substitution of the data into the equation for a second-order rate constant gave values constant to within about 6%.

To obtain an estimate of the absolute magnitude of the second-order specific reaction constant a 12-l. flask, filled with equal volumes of carbon monoxide and hydrogen at atmospheric pressure and containing a known amount of cobalt hydrocarbonyl gas, was kept at 25 ± 1° for five days, after which the amount of undecomposed cobalt hydrocarbonyl was determined. The specific reaction rate constant was found to be 3×10^{-3} (mole/liter)$^{-1}$ second^{-1}. In a similar experiment in which helium was used as a diluent gas, the specific reaction rate constant was found to be of the same order of magnitude.

The relative stability of cobalt hydrocarbonyl in the gas phase compared to that in the liquid phase can now be more readily understood. If it is assumed that the order and rate of the reaction in the liquid phase are the same as those in the gas phase, the half-life of a 1 and a 9 M solution of cobalt hydrocarbonyl may be computed using equation (6)

$$t_{0.5} = 1/ka \qquad (6)$$

where a = initial concentration in moles per liter and k = (mole/liter)$^{-1}$ second^{-1}. Substitution of the value of 3×10^{-3} into equation (6) gives a half-life of 333 seconds for the 1 molar and a half-life of 37 seconds for the 9 molar solution of cobalt hydrocarbonyl. This result is in good agreement with the observation that a 1 M solution of cobalt hydrocarbonyl in hexane decomposes within a few minutes and that liquid cobalt hydrocarbonyl,[7] which is approximately 9 M, is not stable at room temperature.

Behavior of Cobalt Hydrocarbonyl in Aqueous Solution.—To obtain data on the acid strength[8] of cobalt hydrocarbonyl an 0.02 M aqueous solution of cobalt hydrocarbonyl was titrated potentiometrically with 0.1 N aqueous sodium hydroxide at room temperature. The pH of the solution before titration as well as the neutralization curve corresponded to those of a strong acid such as hydrochloric acid. Phenolphthalein was a suitable indicator, whereas methyl orange and methyl red, contrary to published reports,[9] could not be used since these azo-type indicators were immediately reduced by the hydrocarbonyl.

It is rather interesting that, in spite of its acid strength, cobalt hydrocarbonyl is only sparingly soluble in water. The concentration of a saturated aqueous solution of cobalt hydrocarbonyl at room temperature was found to be 5.6×10^{-2} mole per liter.

In aqueous solution and in the absence of oxygen, cobalt hydrocarbonyl is fairly stable at room temperature. After 14 days the molarity of an aqueous solution of cobalt hydrocarbonyl had decreased from 0.0192 to 0.0148; hence, the accuracy of a titration at room temperature is not affected by decomposition of cobalt hydrocarbonyl.

The stability of the aqueous (ionized) solution of cobalt hydrocarbonyl is impressive if it is considered that the half-life of a 0.02 M solution of cobalt hydrocarbonyl in hexane is about 5 hours.

Infrared Spectra of Dicobalt Octacarbonyl, Cobalt Hydrocarbonyl and Cobalt Deuterocarbonyl.—The infrared spectra of dicobalt octacarbonyl in n-hexane and those of cobalt hydrocarbonyl and cobalt deuterocarbonyl in the gas phase are given in Table I.

TABLE I

INFRARED SPECTRA OF $[\mathrm{Co(CO)_4}]_2$, $\mathrm{HCo(CO)_4}$ AND $\mathrm{DCo(CO)_4}$

s = strong; m = medium; w = weak; v = very; sh = shoulder

$[\mathrm{Co(CO)_4}]_2$ in n-hexane (ν, cm.$^{-1}$)	$\mathrm{HCo(CO)_4}$ gas, in helium (ν, cm.$^{-1}$)	$\mathrm{DCo(CO)_4}$[a] gas, in helium (ν, cm.$^{-1}$)
..	2121 (s)	2121 (s)
2066 (s)	2066 (s sh)	2066 (s sh)
2041 (vs)	2043 (vs)	2043 (vs)
2024 (s sh)	2004 (s)	2004 (s)
..	1976 (ms)	1976 (ms)
..	1929 (w)	1929 (w)
1859 (ms)	1869 (w)	1869 (w)
..	703 (s)	703 (s)

[a] 65% deutero-, 35% hydrocarbonyl.

Although cobalt hydrocarbonyl decomposes at room temperature to form dicobalt octacarbonyl (equation 2), in the gas phase spectrum there is no interference except for background scattering because dicobalt octacarbonyl settles out as tiny crystals. In hexane solution, the dicobalt octacarbonyl, as it is formed from the decomposition, dissolves in the solvent and produces its characteristic spectrum. It is of interest to note that the spectrum of this solution on a dicobalt octacarbonyl-free basis, is identical with the gas-phase spectrum of the hydrocarbonyl.

None of the absorption bands found in cobalt hydrocarbonyl can be assigned to a hydrogen linkage with oxygen, carbon or cobalt This was demon-

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(7) W. Hieber, F. Seel and H. Schneider, *Chem. Ber.*, **85**, 647 (1952).

(8) It has been stated[9] that, according to its neutralization curve in aqueous acetone solution, cobalt hydrocarbonyl behaves like a strong acid. However, experimental details leading to this conclusion were not reported.

(9) J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Pub. Corp., New York, N. Y., 1949, p. 289.

strated by the fact that the infrared spectrum of cobalt deuterocarbonyl (65% deutero-, 35% hydrocarbonyl) is identical to that of the hydrocarbonyl in the 2 to 15 μ region. Any band due to a bond between hydrogen and another atom, such as oxygen, carbon or cobalt would shift to longer wave length upon replacement of the hydrogen with deuterium.

The fact that the spectra of $DCo(CO)_4$ and $HCo(CO)_4$ are identical is not necessarily inconsistent with the postulation of an OH bond as suggested by Ewens and Lister.[10] However, if such a bond exists the resulting absorption band would be of very low intensity.

Because of the reactivity and instability at high concentrations of cobalt hydro- and deuterocarbonyl, infrared investigations at higher gas and liquid concentrations or in thicker cells were not carried out. At the concentrations available, there was negligible absorption in the 5.7 to 13.5 μ region. This part of the spectrum was therefore omitted. A study of these spectra at low temperatures where higher concentrations may be feasible is planned, as well as an investigation of the longer wave length regions for evidence of a possible bond between hydrogen and cobalt.

Mass Spectrographic Data.—Mass spectrometric analysis of gaseous cobalt hydrocarbonyl yielded peaks for Co(CO), $Co(CO)_2$, $Co(CO)_3$, $Co(CO)_4$ and hydrogen. Hydrogen was not found as part of any other fragment. In this respect, cobalt hydrocarbonyl differs from chromium hydrocarbonyl where mass spectrometric data indicated[11] the existence of chromium–hydrogen fragments.

Experimental

Preparation of Cobalt Hydrocarbonyl.—Dicobalt octacarbonyl (3.00 g.) is placed in a 300-ml. erlenmeyer flask provided with a ground-glass joint, and 20 ml. of C.P. pyridine is added. The flask is now fitted with a ground joint carrying a U-tube filled with just enough mercury to make a seal. The mercury valve permits the escape of carbon monoxide and prevents access of air to the reaction mixture. The reaction is complete after a few minutes. The pyridine solution containing the salt $[Co(Pyr)_6][Co(CO)_4]_2$ may be stored, provided prolonged exposure to air is avoided. A short exposure to air, such as is required for the transfer of the solution, is not detrimental.

The apparatus for the generation of cobalt hydrocarbonyl consists of a 500-ml., three-necked flask provided with an inlet tube (constricted at the tip to about 1–2 mm.), a dropping funnel, and an outlet tube. To the outlet tube is attached an absorption tube (90 × 30 mm.) filled with phosphorus pentoxide-coated glass beads. The absorption tube is connected to a cold trap (200 × 40 mm.) immersed in liquid nitrogen. The three-necked flask is filled with 75 ml. of water and 25 ml. of concentrated sulfuric acid, and the flask is immersed in an ice-bath. The flask is then fitted with the inlet tube, the dropping funnel, and the outlet tube, and the pyridine solution is poured into the dropping funnel. The dropping funnel and the inlet tube are connected by a T-tube, and the system is purged with carbon monoxide. After purging, the pyridine solution is added dropwise to the reaction flask. The rate of addition is regulated so that most of the oily droplets (cobalt hydrocarbonyl) forming on the surface of the aqueous solution have disappeared before more pyridine solution is added. If the solution is added faster than the hydrocarbonyl is removed by the gas current, losses occur due to decomposition of the hydrocarbonyl in the flask. If the gas flow is too fast, some hydrocarbonyl is carried past the cold trap. Repeated experiments have shown that, with the quantities described above, maximum yields are obtained with a gas flow of about 350 ml. per minute and addition of the pyridine solution (20 ml.) during 45 minutes.

From 3.00 g. of dicobalt octacarbonyl, the yield of pure cobalt hydrocarbonyl is 1.90 g. or 95% of theoretical.

When hydrogen or helium is used in place of carbon monoxide considerable amounts of the tetramer $[Co(CO)_3]_4$ are formed in the reaction flask and the yield of hydrocarbonyl is about 50% of theoretical.

Decomposition of Cobalt Hydrocarbonyl.—A 12-l. round-bottomed flask fitted with a stopper and a three-way stopcock was evacuated and attached to the phosphorus pentoxide tube of the cobalt hydrocarbonyl generator. The apparatus was purged with synthesis gas (equal volumes of carbon monoxide and hydrogen), and the stopcock of the evacuated flask was turned to admit synthesis gas carrying cobalt hydrocarbonyl until the flask was filled (about 35 minutes), whereupon the flask was disconnected. After a few hours, small crystals of dicobalt octacarbonyl began to form on the wall of the flask.

The concentration of cobalt hydrocarbonyl was determined as follows. An evacuated 3-l. flask fitted with a stopper and stopcock was attached to the 12-l. flask, and the pressure was allowed to equilibrate. The 3-l. flask was removed, and a few ml. of aqueous ammonia (concentrated ammonia and water, 1:1) was poured into the stopcock arm of the 3-l. flask. The stopcock was turned carefully to admit the solution to the flask without allowing any air to enter. This process was repeated until about 10 ml. of the ammonia solution had been added to the flask. (Heavy fumes of $NH_4Co(CO)_4$ were formed, similar to those observed on mixing ammonia and hydrochloric acid gas.) The flask was rotated and allowed to stand for 15 minutes in order to distribute the ammonia solution over a large area and to complete the absorption of gaseous cobalt hydrocarbonyl. Then 25 ml. of nickel *o*-phenanthroline chloride solution[12] was added through the stopcock to form the water-insoluble precipitate $[Ni(o\text{-phen})_3][Co(CO)_4]_2$. The flask was shaken for about 1 minute, the stopcock opened, and the stopper removed. About 50 ml. of water was added to the flask, and the amount of $[Co(CO)_4]^-$ in the precipitate was determined by a gasometric procedure.[12] After standing at 25 ± 1° for 112 hours, the flask was sampled again as described.

A second, similar experiment was carried out with helium as the diluent instead of synthesis gas. In this case, black crystals of the tetramer, $[Co(CO)_3]_4$, deposited on the wall of the flask. The second gas sample was taken after the gas had remained at 25 ± 1° for 120 hours. The concentration of cobalt hydrocarbonyl in the 12-l. flask after removal of the first gas sample is given as initial concentration, that before removal of the second sample as final concentration. The rate constants were calculated from $k = [x/a(a - x)]t^{-1}$, where t is the time in seconds, a is the initial and $a - x$ the final concentration in moles/liter. The results of these two experiments are listed in Table II.

Table II

Diluent	Concn., moles of $HCo(CO)_4$/l. $\times 10^4$	Time, hours	Specific reaction rate constant, k, $(mole/l.)^{-1}$ $(sec.)^{-1} \times 10^3$
$1H_2$:1CO	4.45	0	
	2.77	112	3
He	2.39	0	
	1.43	120	6

These results are to be regarded as semi-quantitative, and no special significance should be attached to the difference in rate constants. The accuracy of the sampling and analysis, as well as the degree of temperature control, were only sufficient to give the order of magnitude of the constant.

Acidity and Stability of Cobalt Hydrocarbonyl in Aqueous Solution.—Oxygen-free water (100 ml.) was placed in a 300-ml. erlenmeyer flask fitted with a stopper, an inlet tube reaching to the bottom of the flask, and an outlet tube. Both inlet and outlet tubes were provided with stopcocks.

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(10) R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **35**, 681 (1939).

(11) M. G. Rhomberg and B. B. Owen, This Journal, **73**, 5904 (1951).

(12) H. W. Sternberg, I. Wender and M. Orchin, *Anal. Chem.*, **24**, 174 (1952).

The erlenmeyer flask was attached to the cobalt hydrocarbonyl generator, and cobalt hydrocarbonyl diluted with synthesis gas was bubbled through the flask for about 5 minutes. The flask was removed from the generator and the solution transferred to a buret in an atmosphere of nitrogen. The solution was titrated in a 100-ml. beaker fitted with a stopper provided with holes for two electrodes, a buret and an inlet and an outlet tube. The inlet tube was connected to a nitrogen cylinder, the outlet tube to a mercury valve. By means of this arrangement, an inert atmosphere could be maintained during the titration. The aqueous cobalt hydrocarbonyl solution (25.00 ml.) was measured into the beaker and a buret containing 0.1 *N* sodium hydroxide inserted in the stopper. The following data were obtained at 26° with a Beckman *p*H meter (model H2).

0.1 *N* NaOH, ml.	*p*H	0.1 *N* NaOH, ml.	*p*H	0.1 *N* NaOH, ml.	*p*H
0.00	1.65	4.50	2.69	4.90	8.29
1.00	1.71	4.60	2.99	5.00	8.85
3.50	1.81	4.70	5.45	5.11	9.30
4.00	2.05	4.80	7.61	5.20	9.60

According to these data, the cobalt hydrocarbonyl solution was 0.0192 *M*. The *p*H of 1.65 indicates that the cobalt hydrocarbonyl is completely dissociated. (The *p*H of a completely dissociated 0.0192 *M* solution would be 1.72.) After standing for 14 days at room temperature, the solution was titrated again and found to be 0.0148 *M*.

Neither methyl orange nor methyl red could be used as indicators. They were discolored within a few seconds by both alkaline and acid solutions of cobalt hydrocarbonyl, possibly by reduction of the azo to a hydrazo group. A good indicator is phenolphthalein: Fifty ml. of an aqueous solution of cobalt hydrocarbonyl was titrated with 0.1 *N* sodium hydroxide in the presence of phenolphthalein. After titration, cobalt was determined by addition of ammonia and hydrogen peroxide, followed by treatment with concentrated sulfuric acid and electrolysis of the acid solution. The amount of cobalt determined by titration was 0.1656 g.; that by electrolysis was 0.1665.

The solubility of cobalt hydrocarbonyl in water was determined as follows: an erlenmeyer flask containing 50.0 ml. of distilled oxygen-free water and phenolphthalein indicator was fitted with a buret and an inlet and an outlet tube and attached to the cobalt hydrocarbonyl generator described above. A current of carbon monoxide containing approximately 1 millimole of $HCo(CO)_4$ per liter was bubbled through the water at 25° and a rate of 300 ml. per minute. Cobalt hydrocarbonyl could be detected in the gas stream leaving the erlenmeyer flask 5 minutes after the start of the experiment, and the experiment was continued for 15 minutes after this point had been reached. The flask was detached and the solution titrated with a 0.1 *N* NaOH solution; 28.0 ml. was required for neutralization. Thus the saturated aqueous solution was 5.6×10^{-2} *M* with respect to cobalt hydrocarbonyl.

Preparation of Cobalt Deuterocarbonyl.—One ml. of a pyridine solution containing 0.15 g. of dicobalt octacarbonyl was slowly added to dilute deuterium sulfate (prepared from 2 g. of sulfur trioxide and 4 g. of heavy water)[13] in a microversion of the apparatus described above for the generation of cobalt hydrocarbonyl. The cobalt deuterocarbonyl was swept out with helium and collected in a 500-ml. evacuated flask from which a gas sample was transferred to the gas cell. Mass spectrometric analysis of a similar preparation, in which argon was used instead of helium as the diluent gas, showed that the carbonyl gas consisted of about 35% of hydrocarbonyl and 65% of deuterocarbonyl. Since pure D_2SO_4 was used for the preparation, the presence of $HCo(CO)_4$ in $DCo(CO)_4$ is probably due to exchange reactions with pyridine, but this point was not investigated.

Infrared Spectra.—To obtain the spectra of $HCo(CO)_4$ and $DCo(CO)_4$ in the gas phase, two 10-cm. gas cells were filled at atmospheric pressure with helium containing approximately 0.5 millimole/liter of $DCo(CO)_4$ and $HCo(CO)_4$.

Determination of the spectra of cobalt hydrocarbonyl in hexane was carried out in a 0.1-mm. cell at a concentration of approximately 0.1 *M*. The spectrum of dicobalt octacarbonyl was carried out in a 0.014-mm. cell at a concentration of approximately 0.6 *M*. The spectrum of this solution in a 0.07-mm. cell revealed no additional bands.

The spectra were determined on a Perkin–Elmer Model 21 spectrophotometer.

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[13] J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, THIS JOURNAL, **73**, 5741 (1951).

BRUCETON, PENNA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF KANSAS STATE COLLEGE]

Correlation of Color and Constitution. I. 2,4-Dinitrophenylhydrazones

BY G. DANA JOHNSON[1]

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A method is described whereby $\lambda_{max.}$ of the ultraviolet absorption spectrum may be calculated from the structure of a 2,4-dinitrophenylhydrazone. The method is applicable to D.N.P.'s of all types of aldehydes and ketones, except cyclic ketones.

With reference to the formula of a 2,4-dinitrophenylhydrazone (Fig. 1), it is possible to express $\lambda_{max.}$ as the sum of three quantities: a constant quantity attributed to the central, recurring dinitrophenylhydrazone moiety, and two other quantities attributed to the groups R_1 and R_2. Thus, if the dinitrophenylhydrazone moiety is indicated by *N*, a series of equations of the form

$$\lambda R_1 + \lambda R_2 + \lambda N = \lambda_{max.}$$

can be set up. Further, if attention is directed to those D.N.P.'s in which each R group is repeated in at least two compounds, it is possible by the least squares method to obtain a unique solution for each quantity in the above equation.

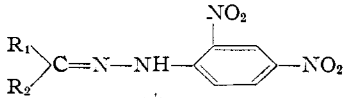

Fig. 1.

A first trial with 104 D.N.P.'s of aromatic, aliphatic and unsaturated aldehydes and ketones gave only fair results. Eighteen per cent. of the compounds gave deviations (obsd. − calcd.) of more than 4 mμ.

Better results came about through a division of the D.N.P.'s into three groups: group 1, diaryl ketones or vinylogs of these; group 2, aryl aliphatic ketones and aromatic aldehydes; group 3, aliphatic ketones and aldehydes. In this manner, values for the various R groups making up the D.N.P.'s and

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[1] Some of this work was carried out at Indiana University.