## Summary

The decreases in volume which occur at 25° when cupric, cobaltous and nickelous cyanates and thiocyanates combine with pyridine to form hexapyridine cyanates and tetrapyridine thiocyanates have been determined.

The shrinkage in cc. during the formation of the hexapyridine cyanates is about 1.74 times as great as during the formation of the tetrapyridine thiocyanates. This corresponds to about 16% more shrinkage for each molecule of pyridine in the complex cyanates than for each molecule in the complex thiocyanates. This fact, and the fact that the complex cyanates have the lower dissociation pressures, both indicate that the pyridine in the complex cyanates is held by greater forces of chemical affinity than in the complex thiocyanates. The thiocyanate radical to a greater extent than the cyanate radical exhausts the total affinity of the metal atom and leaves less of it available for coördinative combination with pyridine.

For the three cyanates and thiocyanates alike, the shrinkage during combination with pyridine is least in the case of the cupric compounds, next in the case of the cobaltous, and most in the case of the nickelous compounds.

CAMBRIDGE, MASS. RECEIVED JULY 28, 1936

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

# The Heats of Dissociation of Hexaarylethanes

BY CHARLES BUSHNELL WOOSTER

In a recent paper Conant[1] has estimated the heats of dissociation of a number of substituted ethanes from cryoscopic data on the basis of the following assumptions: (1) that the heat of dissociation, $\Delta H$, the free energy of dissociation, $\Delta F$, and the corresponding entropy change, $\Delta S$, were all approximately independent of the nature of the solvent in which the ethane was dissolved; (2) that $\Delta H$ and $\Delta S$ were independent of the temperature over the range involved in the experiments and (3) that $\Delta S$ was independent of the substituents attached to the two carbon atoms which dissociate from each other, at least in solution in organic solvents. The work of Ziegler,[2] on hexaphenylethane had furnished confirmation of the first two assumptions, but Conant offered no experimental basis for the third. The last assumption has also been made by Pauling and Wheland[3] but, on the other hand, Hückel[4] states that variations in the entropy change may be expected to accompany alterations in the structure of the molecules.

As a matter of fact, it is possible to calculate values for the heats of dissociation of four hexaarylethanes by independent and somewhat more direct methods from data at present available in the literature. It is the purpose of this paper to present and discuss the results of such calculations.

**The Heat of Dissociation of Di-β-naphthyltetraphenylethane.**—Gomberg and Sullivan[5] have measured the intensity of color of solutions of di-β-naphthyltetraphenylethane over a wide temperature range in toluene and in chloroform solutions. A sufficiently close approximation to the dissociation constant $K$, expressed in mole fractions, may be obtained from these measurements by the use of equation 1

$$K = \frac{4N(I/I_0)^2}{1 - I/I_0} \qquad (1)$$

where $N$ is the concentration in moles of the ethane per mole of solvent, $I$ is the intensity of color per mole of the ethane (in arbitrary units) and $I_0$ is the limiting value of $I$ on dilution.[6] In order to test the consistency of the data, $\Delta H$ is best determined graphically by plotting values of $-\log K$ against $1/T$ which should yield a straight line in accordance with equation 2

$$-\log K = (\Delta H/2.303RT) + \text{const.} \qquad (2)$$

when $\Delta H$ is independent of the temperature. The value $I_0 = 195$ was obtained from equation 1 by setting $K$ equal to the value $3.50 \times 10^{-4}$ based on Ziegler's photometric measurements at 20° in

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[1] Conant, *J. Chem. Phys.*, **1**, 427 (1933).

[2] Ziegler, *Ann.*, **373**, 163 (1929).

[3] Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

[4] Hückel, "Free Radicals, a General Discussion," The Faraday Society, 1933, p. 40.

[5] Gomberg and Sullivan, THIS JOURNAL, **44**, 1810 (1922).

[6] The value of $I_0$ is assumed to be independent of the temperature and of the nature of the solvent. These assumptions were also made by Ziegler in his study of hexaphenylethane.

cyclohexane[7] and substituting the observed value of $I$ at that temperature. A plot of $-\log K$ against $1/T$ appears in Fig. 1. The points obtained in the two solvents lie on the same curve which is linear within the limits of error over a range of 56° in toluene and 52° in chloroform. The value of $\Delta H$ corresponding to the slope of this line is 12.9 kcal.

The method suggested for the estimation of $I_0$ neglects any variation in $K$ which might occur as a result of changing the solvent from cyclohexane to toluene and to chloroform. Some justification for neglecting this variation may be found in the correspondence between the measurements in toluene and chloroform which shows that the values of $K$ in these two solvents do not differ sufficiently to influence appreciably the value of $\Delta H$. However, Ziegler found much wider differences in the values of $K$ for hexaphenylethane in various solvents, so it is necessary to examine carefully the influence of the choice of $I_0$ on the value of $\Delta H$ as calculated from the data of Gomberg and Sullivan.

As a matter of fact, $\Delta H$ is not very sensitive to the choice of $I_0$ when this constant is not too small. The expression for $\Delta H$ may be written

$$\Delta H = RT^2(\mathrm{d}\ln K/\mathrm{d}T) = RT^2\frac{\mathrm{d}}{\mathrm{d}t}[2\ln I - \ln(1 - I/I_0)] \qquad (3)$$

and in the limiting case when $I_0$ is sufficiently great, $1 - I/I_0$ may be replaced by unity so that on integration a linear relation between $\log I$ and $1/T$, similar in form to equation 2, is obtained.

$$-\log I = (\Delta H/4.606RT) + \text{const.} \qquad (4)$$

Plots of $\log I$ against $1/T$ for the $\beta$-naphthyl compound in toluene and in chloroform are actually linear in accordance with equation 4 and the value of $\Delta H$ thus obtained is 12.3 kcal. The term $1-I/I_0$ cannot exceed unity so the neglected term always makes a positive contribution to $\Delta H$ when $I$ increases with the temperature. Therefore, the value 12.3 kcal. may be regarded as a reliable *minimum* within the limits of experimental error, regardless of the true value of $I_0$.[8]

A third method of approximation may be used to set a maximum limit for $\Delta H$. Gomberg and Sullivan also gave data regarding the intensity of color of solutions of the ethane in *cyclohexane* at its freezing point 5.8°. Taking the value of $K$ in cyclohexane at 293°K. as $3.50 \times 10^{-4}$ and using the minimum value of $\Delta H$ = 12.3 kcal., a maximum value of $1.22 \times 10^{-4}$ may be calculated for $K$ in cyclohexane at 279°K. By the use of equation 1 the value of $I_0$ may be determined[9] from the values of $I$ in cyclohexane at 5.8°. Unfortunately, these values of $I$ and consequently the resulting values of $I_0$ are not expressed in the same units as those given for the toluene and chloroform solutions. This difficulty may be circumvented in the following way. From the data on benzene solutions at the freezing point, 5.3°, neglecting the temperature difference of 0.5°, the

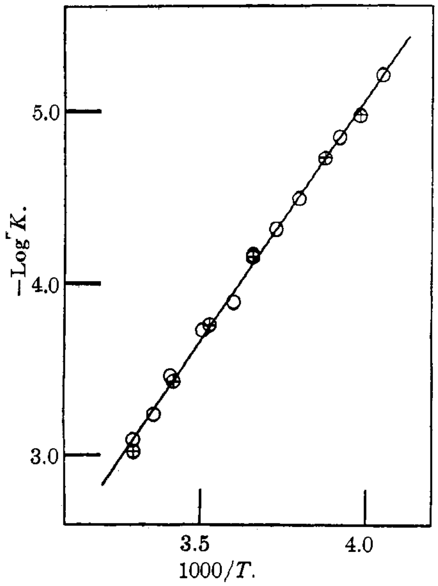

Fig. 1.—Plot of $-\log K$ against $1/T$ for di-$\beta$-naphthyltetraphenylethane in toluene (open circles) and in chloroform (crossed circles).

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(7) This value of the equilibrium constant is somewhat uncertain because Ziegler did not determine the concentration of his solution by direct analysis. The concentration has been estimated from the amount of triarylmethyl chloride used, assuming a theoretical yield of the ethane. Since Gomberg and Sullivan obtained the yields 99.6, 102 and 100% in three quantitative studies of this reaction, it is believed that the error thus introduced is actually quite small; in any event, this value of $K$ in cyclohexane may be regarded as a reliable *maximum*.

(8) The solutions used by Gomberg and Sullivan were about 0.034 molar with respect to the ethane and the values of $I$ increased approximately ten-fold in passing from the lowest to the highest temperature so that the degree of dissociation, $\alpha = I/I_0$, in toluene, calculated on the basis $I_0$ = 195, varies from 0.0205 at −26° to 0.2100 at +30°. Although it may seem a very arbitrary procedure to set $1-\alpha$ equal to unity when $\alpha$ = 0.21, this simplification is justified by the fact that the extreme variation in $1-\alpha$ from 0.979 to 0.790 is accompanied by a variation in $\alpha^2$ from $4.2 \times 10^{-4}$ to $4.4 \times 10^{-2}$ and, accordingly, the neglected variation in $1-\alpha$ contributes but 4.4% of the total variation in $-\log K$.

(9) It has been pointed out previously [Wooster, THIS JOURNAL, 51, 1163 (1929)] that these measurements are not sufficiently accurate to permit the determination of $I_0$ by direct extrapolation because the concentration range is so narrow that the moderate experimental errors are greatly magnified by the process of extrapolation. A similar magnification of the experimental errors is not involved in the direct calculation of $I_0$ from $I$ and $K$.

ratio of $K_b$ (the dissociation constant in benzene) to $K_c$ (the dissociation constant in cyclohexane) may be calculated by the use of equation 5.

$$K_b/K_c = (N_b/N_c)(I_b/I_c)^2(I_0 - I_c)/(I_0 - I_b) \quad (5)$$

where $I_b$ and $I_c$ are the color intensities in the respective solvents corresponding to the concentrations (in moles ethane per mole solvent) $N_b$ and $N_c$. The three available intercomparisons yield the value $K_b/K_c = 1.14 \pm 0.06$.

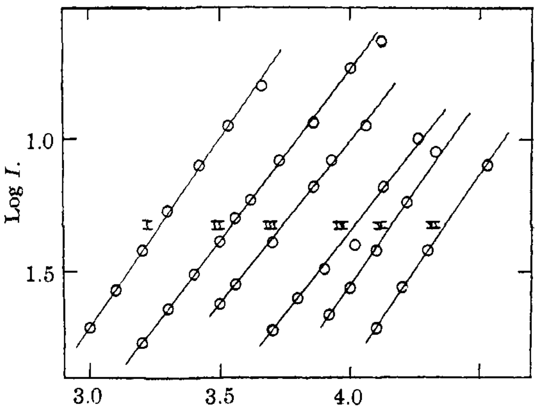

Fig. 2.—Plot of log $I$ against $1/T$ for symmetrical tetramethoxyhexaphenylethanes. Curve I is plotted with respect to the horizontal scale given. Each succeeding curve is displaced two-tenths of a unit to the right with respect to this scale. The vertical scale is the same for all six curves: I, the 2,5-compound in toluene; II, the 2,5-compound in bromobenzene; III, the 3,4-compound in bromobenzene; IV, the 3,4-compound in toluene; V, the 2,4-compound in toluene; VI, the 2,4-compound in bromobenzene.

Since the color intensities of the toluene solutions (concentration 2 g. per 100 cc.) were determined by matching a 17-mm. column against a column of a standard solution of the same free radical in benzene (concentration 0.5 g. per 100 cc.) at room temperature (21–22°) and the diameters of the two tubes of the colorimeter were equal, the ratio $K_t/K_b$ ($K_t$ = the dissociation constant in toluene) at this temperature may be calculated from these data by using a simplified form of equation 5.

$$K_t/K_b \overset{=}{<} (N_t/N_b)(I_t/I_b)^2 \quad (6)$$

The simplification is possible because at the temperature in question $I_t < I_b$ so that $(I_0 - I_b)/(I_0 - I_t)$ is less than unity; consequently the simplified expression yields a *maximum* value for $K_t/K_b$ at that temperature. The value of $I_t/I_b$ is equivalent to the height of the benzene solution divided by four times the height of the toluene solution, since the latter contains four times as much solute as the former. At 22° the height of the benzene solution would be 30 mm.[10] so $K_t/K_b \overset{=}{<} 0.925$. If $\Delta H$ is independent of the nature of the solvent $K_b/K_c$ will have the same value at 22° as at 6° and $K_t/K_c \overset{=}{<} 1.06 \pm 0.06$. The maximum variation in $\Delta H$ due to the nature of the solvent observed by Ziegler with hexaphenylethane was 1.5 kcal. Assuming that $\Delta H$ for the $\beta$-naphthyl compound in benzene exceeds by 1.5 kcal. the value in cyclohexane, the ratio $K_b/K_c$ would become $1.32 \pm 0.07$ at 22° so it is reasonable to conclude that $K_t/K_c$ does not exceed 1.30 at the latter temperature. The difference between this ratio and the value of unit previously assumed is negligible for the purpose of calculating $\Delta H$ since it changes the result by less than 0.1 kcal. Therefore, as far as uncertainties in the value of $I_0$ are concerned $\Delta H$ for the $\beta$-naphthyl compound probably lies between the limits 12.3 and 12.9 and, making allowance for experimental error, it may be taken as $12.9 \pm 1$.[11]

**The Heats of Dissociation of Tetramethoxyhexaphenylethanes.**—Similar colorimetric measurements have been made by Gomberg and Forrester[12] with three symmetrically substituted tetramethoxyhexaphenylethanes. A plot of log $I$ against $1/T$ appears in Fig. 2. The curves are nearly linear at the higher temperatures and the slopes correspond to the following *minimum* values of $\Delta H$ in kcal.: di-(2,5-dimethoxyphenyl)-tetraphenylethane in toluene 12.8, in bromobenzene 11.6; di-(3,4-dimethoxyphenyl)-tetraphenylethane in toluene 11.4, in bromobenzene 11.3; di-(2,4-dimethoxyphenyl)-tetraphenylethane in toluene 12.7, in bromobenzene 13.0. The measurements at the lower temperatures have been disregarded because when the color intensities are low the experimental errors produce larger deviations in the plot. The behavior of the 2,4-compound in bromobenzene is exceptional, the color intensities, for some unexplained reason, pass through a minimum at about 5° and rise rapidly

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[10] Obtained from the value 28 mm. at 20° by interpolation using the *experimentally* observed linear relation between log $I$ and $1/T$.

[11] The temperature of the standard benzene solution was not given directly by Gomberg and Sullivan who stated that it was at "room temperature." In order to obtain the most probable value for the ratio $K_t/K_b$, the value 21–22° for the room temperature given elsewhere in the same paper has been used. However, it is practically certain that the temperature of the standard did not exceed 30°, the highest temperature employed in the measurements. Since at that temperature the height of the standard was 41 mm., $(K_t/K_b)_{303} \overset{=}{<} 1.73$, $(K_t/K_c)_{303} \overset{=}{<} 2.56$, $(K_t/K_c)_{293} \overset{=}{<} 2.78$ and $\Delta H \overset{=}{<} 13.3$, which is within the limits of error of the final value.

[12] Gomberg and Forrester, THIS JOURNAL, **47**, 2373 (1925).

at lower temperatures. Nevertheless, the measurements above 10° yield a linear plot and correspond to the same value of $\Delta H$ as those made in toluene where the color intensities do not exhibit a minimum. In any event, the discrepancies at low temperatures cannot be ascribed to the failure of the approximation involved in equation 4, because such effects would be most pronounced at the higher temperatures.

## Discussion of Results

The averaged values of $\Delta H$ are collected in Table I together with the corresponding values $\Delta H^*$ estimated according to Conant's method by setting $\Delta S = 17$ E. U. in the expression[13]

$$\Delta H = \Delta F + T\Delta S \qquad (7)$$

TABLE I

HEATS OF DISSOCIATION OF HEXAARYLETHANES–TETRAPHENYL SERIES OF THE GENERAL FORMULA

$(C_6H_5)_2\underset{R}{C}-\underset{R}{C}(C_6H_5)_2$

| R | $\Delta H$, kcal. | $\Delta H^*$, kcal. | $\Delta F$, kcal. | $\Delta S$, E. U. |
|---|---|---|---|---|
| β-Naphthyl | 12.9 | 8.9 | 4.5 | 28 |
| 2,5-Dimethoxyphenyl | 12.2 | 9.3 | 4.4 | 26 |
| 3,4-Dimethoxyphenyl | 11.3 | 9.3 | 4.3 | 23 |
| 2,4-Dimethoxyphenyl | 13.9 | 9.4 | 4.6 | 28 |

The values of $\Delta H^*$ are all low and the actual discrepancies for the methoxy compounds may be even greater, since values of $I_0$ sufficiently low to alter appreciably the values of $\Delta H$ based on equation 4, would correspond to *higher* values of $\Delta H$ and *lower* values of $\Delta F$. The discrepancies may be due in part to errors inherent in the cryoscopic method of determining $\Delta F$, but use of the value of $\Delta F$ for the β-naphthyl compound computed from Ziegler's photometric measurements reduces the difference between $\Delta H$ and $\Delta H^*$ by only 0.6 kcal. The value of $\Delta S = 17$ is approximately the mean value for hexaphenylethane; the extreme limits in the nine different solvents investigated by Ziegler, obtained by combining the highest $\Delta F$ with the lowest $\Delta H$ and *vice versa*, are 12.4 and 22.5. Since all of the values in Table I exceed the highest limit, it seems likely that the entropy of dissociation is not entirely independent of structural influences.

For the sake of completeness, a number of assumptions have been introduced in order to estimate the most probable value of $\Delta H$ for the β-naphthyl compound. However, the *minimum* values based on equation 4 are dependent on but two assumptions, namely, that the variations in color are due to a simple binary dissociation of colorless ethane molecules into colored free radicals (equation 1) and that $I_0$ is independent of the temperature. Of course, the conclusions drawn from these values are subject to the validity of these two assumptions, but, since the same two assumptions are involved in all of Conant's calculations, the minimum values of $\Delta H$ may properly be employed to test whether or not the results of Conant's method are entirely consistent with *all* the assumptions which he has made. Furthermore, Ziegler has shown that the absorption of the β-naphthyl compound is actually in quantitative agreement with the requirements of a binary dissociation over a dilution range of approximately 100–8850 liters in cyclohexane at 20°.

**Pauling and Wheland's Theory.**—Pauling and Wheland[3] have suggested that the low heats of dissociation of the hexaarylethanes are due entirely to a stabilization of the free radicals by resonance[14] and pointed out that the dissociation qualitatively paralleled the calculated resonance energy for a number of substituted ethanes as was to be expected if these ethanes had the same entropy of dissociation. It has just been shown that this condition may not be generally fulfilled.

They took 84 kcal. as the heat of dissociation of the normal C–C bond and gave the values 1.1078 $\alpha$ and 1.1715 $\alpha$ for the resonance energies of the triphenylmethyl and diphenyl-β-naphthylmethyl radicals, respectively. The symbol $\alpha$ represents the single exchange integrals involving adjacent atoms which are necessarily equal for the symmetrical benzene molecule and have been assumed equal in all other molecules. Using Ziegler's value of $\Delta H$ for hexaphenylethane in solution, Pauling and Wheland found $\alpha = -32.8$ kcal., in rough agreement with values of $\alpha$ from other sources. Since this experimental evidence[2] also presupposes the independence of $T$ and $I_0$, it is a fair test to compare the value 7.0 kcal., calculated according to Pauling and Wheland's method for the β-naphthyl compound, with the experimental minimum value 12.3 kcal. This discrepancy certainly casts doubt on the significance of the rough agreement in the values of $\alpha$ noted above. As a matter of fact, Ziegler's studies on pentaphenylcyclopentadienyl[2] indicate that the varia-

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(13) The value of $\Delta H^*$ for the β-naphthyl compound is taken from Conant's paper and was based on $\Delta F$ as calculated from Gomberg and Sullivan's cryoscopic data in naphthalene solution. The other values have been calculated in the same manner from the cryoscopic data of Gomberg and Forrester in dichlorobenzene.

(14) See, however, Bent and co-workers [THIS JOURNAL, 57, 1242 (1935); 58, 165, 170 (1936)] for evidence regarding the importance of other factors than resonance.

tion of the absorption curve with the temperature is not sufficient to affect the values of $\Delta H$ 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-naphthyltetraphenylethane 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-naphthyltetraphenylethane in solution does not agree with the value calculated on the basis of Pauling and Wheland's resonance theory.

PROVIDENCE, R. I. RECEIVED MAY 5, 1936

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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 Windsor[1] in summarizing the properties of the volatile carbonyls, nitrosyl carbonyls and carbonyl hydrides of the metals, noted that in the volatile $CoNO(CO)_3$ the total of the atomic numbers is the same as in the volatile $Ni(CO)_4$; also that in the suspected volatile $HCo(CO)_4$ the same total of atomic numbers prevails.

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

$$Br_2 + Ni(CO)_4 \longrightarrow NiBr_2 + 4CO$$
$$Br_2 + CoNO(CO)_3 \longrightarrow CoBr_2 + NO + 3CO$$

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 Schubert[2] 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, $HCo(CO)_4$, in pure form and contribute to a knowledge of its properties.

Windsor and Blanchard[3] and Blanchard, Rafter and Adams[4] 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 R = [$-CH_2CHNH_2COO-$]:

$$CoCl_2 + 2HSRH{\cdot}HCl + 6KOH \longrightarrow K_2Co(SR)_2 + 4KCl + 6H_2O$$
$$9K_2Co(SR)_2 + 8CO + 2H_2O \longrightarrow 6K_3Co(SR)_3 + 2HCo(CO)_4 + Co(OH)_2$$
$$K_3Co(SR)_3 + 6CO + 7KOH \longrightarrow HCo(CO)_4 + 2K_2CO_3 + 3K_2RS + 3H_2O$$

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

$$2CoCl_2 + 12KOH + 11CO \longrightarrow 2KCo(CO)_4 + 3K_2CO_3 + 4KCl + 6H_2O \quad (1)$$

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 $KCo(CO)_4$, and noted that a very bad odor was produced and that crystals separated which he identified as the dimeric cobalt tetracarbonyl $Co_2(CO)_8$. He was unable to detect either free hydrogen or any product to account for the hydrogen liberated from the postulated hydride $HCo(CO)_4$.

## Experimental

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

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(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).