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The Significance of the Hydrides of the Carbonyls of Iron and Cobalt

BY ARTHUR A. BLANCHARD AND MANLY M. WINDSOR

The existence of unstable hydrides of iron and cobalt carbonyls of the composition $Fe(CO)_4H_2$ and $Co(CO)_4H$ has been very clearly indicated by recent researches of Schubert,[1] Feigl and Krumholz,[2] Hock and Stuhlmann,[3] and Hieber[4] and collaborators. Although these hydrides are so unstable that they have not as yet been isolated and analyzed, their alkali and barium salts are quite easily obtained in water solution, in which condition they are fairly stable and, as far as shown, have unmistakably the properties of well-defined salts. The mercury and silver salts can be precipitated from such solutions and have been analyzed. The hydrides themselves are volatile and, when they are formed by adding acids to solutions of the salts, appear to escape freely as vapors. The cobalt carbonyl hydride is very unstable and immediately undergoes rearrangement so that the undecomposed vapor cannot be collected for identification. The iron carbonyl hydride can be blown from a mixture of $HgFe(CO)_4$ and HI, or from an acidified aqueous $BaFe(CO)_4$ solution in a current of nitrogen into a mercury salt solution where the same mercuric salt is precipitated and can be identified.

It is significant that nickel has not been found to form such hydrides or salts, nor does it form polymers like $(Co(CO)_4)_2$ nor polymers of a lower carbonyl like $(Fe(CO)_4)_3$.

Langmuir[5] in 1921 first suggested that the volatile carbonyls represent a type in which the metal atom takes on the number of electrons necessary to reach the number of the next inert gas, nickel taking on eight electrons in $Ni(CO)_4$, iron ten in $Fe(CO)_5$, and molybdenum twelve in $Mo(CO)_6$.

Reiff[6] in 1931 applied the conception of "effective atomic number"[7] to a study of the carbonyls: CO groups add two electrons and NO groups three to the central atom, and the compound becomes self-contained and volatile when the effective atomic number of the central atom becomes that of the next inert gas. Neither Langmuir nor Reiff specified the arrangement of electrons nor even the number shared. Blanchard and Gilliland in 1926,[8] proceeding from the conviction that the peculiar properties of the carbonyls must arise from some unique electron arrangement, arrived at a pattern which, whatever its defects, uniformly fitted all the volatile carbonyls. It is equally effective in accounting for the existence of the carbonyl hydrides.

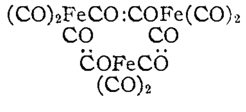
Since nickel carbonyl is without doubt the most completely self-contained of the carbonyls, it is a fair assumption that the self-contained pattern consists of a central atom directly linked to four carbonyl groups. In $Fe(CO)_5$ one carbonyl group and in $Cr(CO)_6$ two carbonyl groups would simply bridge across the outer ends of two of the inner carbonyl groups.

Nickel tetracarbonyl has the requisite number of electrons to give the saturated structure. Neutral monomolecular cobalt tetracarbonyl would lack one electron, but the electron is supplied by hydrogen in $HCo(CO)_4$, and the $Co(CO)_4^-$ ion of the salt $KCo(CO)_4$ has a structure identical to that of nickel carbonyl. In the dimeric cobalt tetracarbonyl the complete complement of electrons is effected through the sharing of one pair by two carbonyl groups:

$$(CO)_3CoCO:COCo(CO)_3$$

In cobalt nitrosyl tricarbonyl $CoNO(CO)_3$, since NO supplies one more electron than CO, we have the same structure as $Ni(CO)_4$.

Monomolecular iron tetracarbonyl would lack two electrons of the saturated molecule. These are supplied by two hydrogen atoms in the volatile $H_2Fe(CO)_4$, and in the ion $Fe(CO)_4^{=}$ we again have the $Ni(CO)_4$ structure. In trimeric iron tetracarbonyl the complete complement is effected by the sharing of three pairs in a cyclic arrangement.



$$\begin{array}{c}(CO)_2FeCO:COFe(CO)_2\\ CO\qquad\quad CO\\ \ddot{C}OFeC\ddot{O}\\ (CO)_2\end{array}$$

The iron atom of iron pentacarbonyl gets its full complement of electrons from five CO groups,

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[1] Schubert, THIS JOURNAL, **55**, 4563 (1933).

[2] Feigl and Krumholz, *Monatsh.*, **59**, 314 (1932).

[3] Hock and Stuhlmann, *Ber.*, **61**, 2097 (1928); **62**, 431, 2690 (1929).

[4] Hieber and Leutert, *Z. anorg. allgem. Chem.*, **204**, 155 (1932).

[5] Langmuir, *Science*, [N. S.] **54**, 59 (1921).

[6] Reiff, *Z. anorg. allgem. Chem.*, **202**, 375 (1931).

[7] Sidgwick, "Electronic Theory of Valency," 1929.

[8] Blanchard and Gilliland, THIS JOURNAL, **48**, 872 (1926).

but the saturated structure of all five carbonyl groups is attained not by all five sharing uniformly with the iron atom, but by four sharing, as in the $Fe(CO)_4^=$ ion, and the fifth bridging across two of the four. Similarly chromium hexacarbonyl[9] and molybdenum hexacarbonyl have two such bridges.

Cobalt trinitrosyl, $Co(NO)_3$, predicted by Reiff on the basis of the effective atomic number, should not be capable of existence if the symmetry of four groups attached to the central atom is an essential part of the stability of the electron distribution. Indeed, Blanchard, Rafter and Adams[10] failed completely to obtain such a substance under conditions that produced the nitrosyl tricarbonyl freely.

Summary

The existence of the hydrides of the carbonyls lends strong confirmation to the thesis that the electron pattern of nickel carbonyl is repeated in all the volatile carbonyls, the addition of hydrogen to the other carbonyls furnishing the number of electrons necessary to complete that pattern. In nitrosyl carbonyls and polymeric carbonyls the same electron pattern is completed.

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[9] Windsor has just determined the vapor density of chromium hexacarbonyl, and found that it corresponds to that of the single molecule $Cr(CO)_6$ [THIS JOURNAL, **56**, 823 (1934)].

[10] Blanchard, Rafter and Adams, *ibid.*, **56**, 16 (1934).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A Series of Simple Basic Indicators. III. The Zero Point of the Acidity Function Scale

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In proposing an acidity function by means of which the "acidity in terms of a basic indicator" may be measured, Hammett and Deyrup[1] pointed out that the most desirable basis for a zero point of this scale would be one which would make the acidity function approach the P_H in infinitely dilute aqueous solution. Because their work was concerned with acidities outside the range of the "dilute aqueous solution," they did not carry out the measurements necessary to establish this zero point and based their scale tentatively upon figures available in the literature for the base strengths of *p*-nitraniline and *o*-nitraniline. In the paper immediately following this it is shown that the transition range from "dilute aqueous solutions" to moderately concentrated solutions of strong acids is especially interesting for the problem of acid catalysis. It is therefore desirable to establish this zero point accurately and finally.

For this purpose we have extended the stepwise intercomparison method of Hammett and Deyrup by the addition of two stronger bases, benzeneazodiphenylamine and aminoazobenzene, whose ionization has been measured colorimetrically in solutions of hydrochloric acid so dilute that the activity of hydrogen ion may be set equal to the molarity of the acid, or, in the more concentrated solutions, to the mean ionic activity. The strength constants, pK', of the new stronger bases follow immediately from the measurement of their degree of ionization in the dilute acid solutions by the equation[1]

$$pK' = -\log (C_{OH_3^+}C_B/C_{BH^+})$$

Since moreover the range of acidity in which they may be used overlaps that of *p*-nitraniline, a value for the pK' of the latter may be obtained by direct comparison of the strengths. The corrected value of pK' for *p*-nitraniline thus obtained serves as a basis for the correction of all of the pK' and H_0 values of Hammett and Deyrup to the new basis.

The present paper also contains measurements of the acidity functions of hydrochloric and nitric acids up to moderate concentrations and of other solutions of interest for the acid catalysis problem.

Materials and Method

For the work with the aminoazobenzene derivatives it was necessary to modify the method of Hammett and Deyrup because these are two color indicators and because of the low acidities in question. A measured number of drops, about 0.15 cc., of an ethyl alcoholic solution of the indicator was added to 25 cc. of the solution to be

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[1] Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932).