Reaction between Iron Pentacarbonyl and Ammonia under High Pressure of Carbon Monoxide

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A recent investigation1) showed that in the presence of iron pentacarbonyl, carbon monoxide under high pressure reacted readily with mono- and dimethylamines at 120°C to produce their formamides, but not readily with ammonia at this temperature. However the reaction with ammonia has now been found to take place at further raised temperatures, resulting in a pale yellow powdery product.

The subject matter of this paper is the reaction conditions for obtaining high yields in the powder, and also the chemical composition of the powder. Suitable conditions for the reaction has permitted us to obtain the yield so high as 90 per cent of the theoretical yield from iron pentacarbonyl used, and the powder has appeared to be a complex ferrous salt containing a complex anion of new composition consisting of CN, CO and NH_3 besides iron.

In addition, the reaction products (powder and simultaneously formed liquor) have been found capable of accelerating the formation of formamide from carbon monoxide and ammonia under high pressure.

Synthesis of Ferrous-Ammine Salt of Carbonyl-Ammine-Ferro-Cyanide

Measured amounts of iron pentacarbonyl and anhydrous ammonia were placed in a 1.1 l. shaking autoclave, and thereafter compressed carbon monoxide was admitted to a required pressure for reaction. The autoclave was kept at a certain temperature for five hours before it was allowed to cool. No reaction occurred at temperatures lower than 150°C, at which a small quantity of pale yellow powder was produced. At a high temperature of 180°C and under the certain reaction conditions nearly all of the iron pentacarbonyl could be converted into the powder and simultaneous liquor*.

The powder was practically insoluble in water, dilute acid and organic solvents such as methanol and ether, but was soluble in caustic potash solution to result in a yellow solution by developing ammoniacal odour and leaving yellowish brown precipitates of, probably, ferrous hydroxide. This solution revealed characteristic reactions of carbonyl-ferro-cyanide ion, $(Fe(CO)(CN)_5)^{3-}$ according to J. A. Müller2), namely it produced a violet precipitate, when acidified and added a solution of ferric chloride, but formed no precipitate with lead acetate and acetic acid.

Conditions for Manufacture of the Powder.—Reactions were run first at a fixed mixing ratio of iron pentacarbonyl to ammonia, under varying pressures of carbon monoxide, secondly at different mixing ratios under a definite pressure of carbon monoxide.

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1) H. Uchida and K. Bando, *J. Chem. Soc. Japan* (*Ind. Sect*)., 57, 941 (1954).

* With respect to the liquor a description will be made later.

2) refer to Gmelin, "Handbuch der Anorganische Chemie", 8te Aufl. Eisen Teil B, 740.

Under initial total pressures* varying from 10 to 155 kg./cm² (at room temperature), a mixture comprising 40 g. ammonia (2.35 M) and 50 g. iron pentacarbonyl (0.25 M) was brought into reaction at 175–185°C. The results are summarised in Fig. 1. At the low pressures the reaction proceeded accompanying the decomposition of iron pentacarbonyl; however, the reaction gave only a small amount of CN, even though it gave a somewhat large amount of the powder. The greatest amount of powder as well as CN was produced at the initial pressure of 70 kg./cm², above which the powder decreased in amount but the quantity of unchanged iron pentacarbonyl increased with ascending pressures.

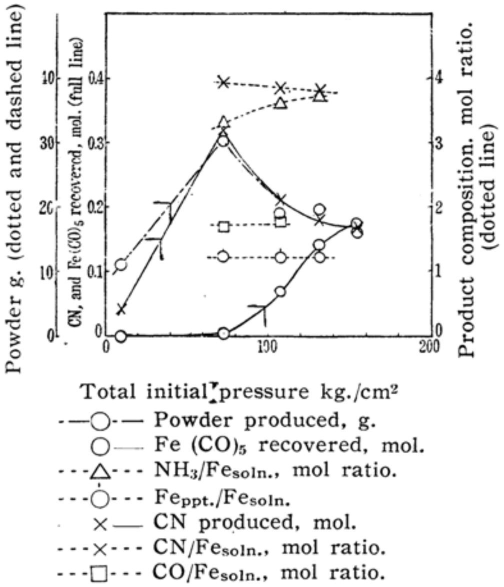

Fig. 1 Effect of total pressure upon yield and composition of product.

As shown in Fig. 1 the ratios $Fe_{ppt.}/Fe_{soln.}$, $CN/Fe_{soln.}$, and $CO/Fe_{soln.}$ . . . the first being the ratio of iron found in precipitate resulted from soaking of the powder in a caustic potash solution to that dissolved in the solution, the second the mol ratio of CN in the powder to iron dissolved, and the third the mol ratio of CO in the powder to iron dissolved . . . were kept at nearly constant levels respectively, throughout the range of pressures employed in the present experiments. On the other hand the values of $NH_3/Fe_{soln.}$, indicating the mol ratio of ammonia found in the powder to iron in the solution, were not found so constant as the above, tending to approach toward 3.75 with the increasing pressures.

The powder was quantitatively analyzed for CN, NH_3 and CO contents. CN content was determined by applying Liebig's method to HCN liberated by the decomposition of the powder with boiling 2-N-sulfuric acid in the presence of cuprous chloride as a catalyst. Ammonia was liberated by prolonged boiling of the powder in caustic potash solution under simultaneous aeration, and was determined by the conventional method*. CO content was determined according to the method by W. Hieber et al.[3], namely the powder was heated to 120–190°C with 70% sulfuric acid in an atmosphere of carbon dioxide, and liberated carbon monoxide was collected in an azotometer. The amount of CO originally contained in the powder could be evaluated by subtracting already determined CN content from the amount of carbon monoxide thus measured in the azotometer, since both CN and CO in the powder were to be obtained as carbon monoxide by this procedure*.

Another inquiry was made for effects of quantities of ammonia upon the yield and composition of the powder by using 50 g. of iron pentacarbonyl under approximate total pressures ranging from 105 to 113 kg./cm². The results are shown in Fig. 2. The figure reveals a tendency for the

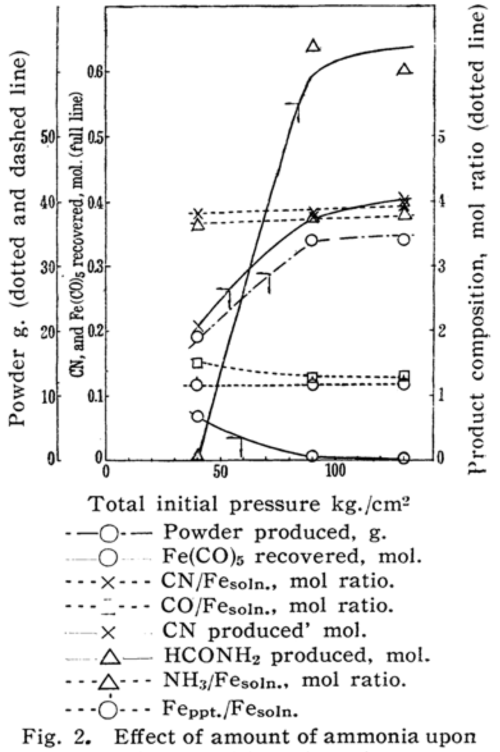

Fig. 2. Effect of amount of ammonia upon yield and composition of product.

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* The total pressure means the sum of pressures of ammonia and the introduced gas comprising 80-81% CO, 15-16% H_2, and 4-5% N_2. After the reaction the pressure increased to 33 kg./cm² in the case of initial pressure of 10 kg./cm² (corresponding to vapour pressures of ammonia at room temperature without the presence of carbon monoxide), but decreased in the other experiments, more markedly with the increasing initial pressures. Hydrogen became richer in the gaseous product than in the initial gas.

* Total nitrogen content was, on the other hand, determined by means of Kjehldahl's method, and was found to be in agreement with the sum of nitrogen determined as CN and NH_3 respectively.

[3] W. Hieber, R. Nast et al., *Z. anorg. allg. Chem.*, **272**, 32 (1953).

* Similarly the usual combustion method also gave the total carbon content which agreed comparatively well with the value here obtained.

powder to increase in amount with the increasing amounts of ammonia up to a yield of 90 per cent of the theoretical yield from iron pentacarbonyl used. The larger amount of ammonia also fayoured the formation of formamide.

In Fig. 2, $Fe_{ppt.}/Fe_{soln.}$, $CN/Fe_{soln.}$ and $NH_3/Fe_{soln.}$ were kept at nearly constant respective values of 1.2, 3.9 and 3.7 independently of the varying quantities of ammonia, and also $CO/Fe_{soln.}$ a value of 1.3 except for the case where a comparatively small amount of ammonia was used. The ratio of $CO/Fe_{soln.}$ attained, on the other hand, to a higher value of 1.75 as illustrated in Fig. 2 and further 2.0 when the greater amount of iron pentacarbonyl was employed*. In these cases part of iron pentacarbonyl, more or less according to the reaction condition, remained unchanged in the reaction.

Composition of the Powder.—From the results of analyses the powder seemed likely to have a practical chemical composition $Fe_2(CN)_4(CO)(NH_3)_4$, of which one half of iron, all of (CN) as well as (CO), and part of (NH_3) could be dissolved in potash solution. The crude powder itself was insoluble in most of the solvents and could not therefore be further purified by recrystallization. However, its caustic potash solution permitted recrystallization to separate out the fine crystal which was presumably a potassium salt of the complex anion.

W. Hieber et al. had described a convenient way for purification of their sodium-carbonyl-ferro-cyanide. The method, when followed in our experiment, produced a mass of fine yellow prismatic crystals. From the results of analyses for CN, CO, NH_3 and iron, conducted as described in the foregoing section, and also for K as its sulfate, the crystal appeared to have a compositon $K_2(Fe(CN)_4(CO)(NH_3))\cdot 1.5H_2O$. Considering this composition in conjunction with the composition $Fe_2((CN)_4(CO)(NH_3)_4)$ of the powder, the powder seems to consist of a complex anion $(Fe(CN)_4(CO)(NH_3))^{2-}$ and a complex cation $(Fe(NH_3)_3)^{2+}$**.

Potassium salts of the powders of two different compositions $Fe_2(CN)_4(CO)(NH_3)_4$ and $Fe_2(CN)_4(CO)_2(NH_3)_3$ (hereafter, simply denoted by A and B respectively) were recrystallised from caustic potash solutions. The powder A was the usual product of the present expertment while the powder B was produced in the particular case where iron pentacarbonyl was used in excess as compared with ammonia.

The procedure for recrystallization of potassium salt of powder A was as follows. A quantity (10 g.) of powder A was soaked in a sufficient, but not too excessive amount (38 g.) of an ice-cooled 10% caustic potash solution to replace one half of the iron (ferrous) with potassium. The yellow filtrate of this solution was then added 300 cc. of ethanol to deposit pale yellow precipitate, which was readily washed with ethanol. The precipitate was further recrystallised in the same way from the aqeous solution, and the recrystallised deposit was dissolved in the possible least amount of water for complete dissolution. The aqueous solution was subsequently allowed to stand for two days in a vacuum-dessicator containing concentrated sulfuric acid, to separate out a mass of fine prismatic crystals (6.5 g.). All the processes were conducted in a dark place in order that the decomposition due to light might be prevented.

The results of analyses of this crystal are given in mol ratios of N, CN etc. to Fe, and they are in good agreement with the composition $K_2(Fe(CN)_4(CO)(NH_3))\cdot 1.5H_2O$, as shown below.

(Total N)/Fe$=4.99\pm0.02$,
(Total C)/Fe$=5.05\pm0.02$,
CN/Fe$=3.95\pm0.01$,
NH_3/Fe$=1.1\pm0.03$, and K/Fe$=1.95$.

	Fe	N	C	CN	NH_3	K wt. %
Calculated from the above formula						
	18.00	22.58	19.36	33.55	5.49	25.21
Observed						
	18.01	22.53	19.54	33.20	5.35	24.59
	18.05	22.61	19.61	33.10	—	—

When the powder B was purified in the same way, the yield in crystalline product was somethat low (4.0 g. from 10 g. of powder B) and the product was proved to have the same composition as that of the product from powder A. The product did not involve second CO. The second CO of the powder may be less stable in the caustic potash solution, otherwise any complex compound containing two CO's, even if it were present in the solution, does not easily sparate out from the solution. No decisive conclusion has yet been given in this respect.

With regard to the complex compound of iron containing CN and CO, J. A. Muller[2)] had already obtained a compound having a composition $K_3(Fe(CN)_5(CO))$ by reacting carbon monoxide on potassium ferrocyanide, and thereafter W. Hieber et al.[3)] could produce a compound of this kind with a high yield of 90 per cent of the theoretical yield from $Na_3(Fe(CN)_5(OH_2))$ used as starting material. The latter[4)] described also the other compound $Fe(CN)_2(CO)_2Py$, where Py represents pyridine. The complex compound obtained in the present work has a different composition from the above compounds and moreover its manufacturing procedure is characterised by the use of iron pentacarbonyl and ammonia as starting materials.

Formamide Formation in Presence of the Reaction Product

Among the results shown in Fig. 2, those

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* In this case the reaction was conducted under a total pressure of 70 kg./cm², by employing 40 g. NH_3 and 200 g. iron pentacarbonyl.

According to W. Hieber and E. Fack (*Z. anorg. allg. Chem.*, **236**, 83 (1938).), the cation should theoretically be $(Fe(NH_3)_6)^{2+}$, but it easily liberates part of ammonia.

4) W. Hieber and F. Sonnekalb et al., *Ber.*, **63**, 982 (1930).

* In the reaction between carbon monoxide and ammonia at high pressure ammonium carbamate was customarily produced (refer to K.H. Meyer et al., *Ber.*, **54**, 1708 (1921)).

** Urea was determined by the amount of precipitate produced by addition of xanthydrol.

obtained with excessive amount of ammonia suggested a considerably easy formation of formamide in the presence of the reaction products (powder and liquor). This was reexamined by a succeeding reaction between ammonia and carbon monoxide, both being admitted newly in the autoclave immediately after only the gaseous products had been purged out. Actually the reaction proceeded more rapidly than it did without the presence of reaction products.

Results of the further experiments along this line are listed in Table I. The formation of formamide could be accelerated neither by the presence of the liquor-free powder nor by that of formamide (Exp. No. 1 and No. 2), but was accelerated markedly by the presence of the brown liquor of the crude reaction products (Exp. No. 3). Eighty grams of the liquor involved 41.7 g. formamide, 19.3 g. ammonium carbamate*, 1.1 g. iron and 8.9 g. urea**, among which urea was felt as promising the accelerating effect. The effect was actually realized (Exp. No. 4) and the accerelating action of the reaction product may be ascribed to urea.

TABLE I

EFFECT OF THE REACTION PRODUCT UPON FORMATION OF FORMAMIDE

Exp.*	NH_3	Additive	Initial Pres. (room temp.)	End Pres. (room temp.)	Gas after Reaction		Increase in $HCONH_2$
					CO	H_2	
	g.	g.	kg./cm^2	kg./cm^2	%	%	g.
No. 1	80	$HCONH_2$ 45	117	110	73.0	21.2	≒0
No. 2	80	Powder 35 $HCONH_2$ 45	130	116	69.8	21.2	≒0
No. 3	80	Liquor 80	115	77	51.8	39.6	27
No. 4	80	Urea 25 $HCONH_2$ 45	115	81	60.8	29·4	31.3

* All the experiments were conducted for five hours, at 175–185°C.

The crude powder is insoluble in most of solvents, and can not therefore be further purified by recrystallisation, while a potassium salt of the complex anion has been crystallized from its caustic potash solution, in yellow fine prismatic crystals, which have appeared to have the composition $K_2(Fe(CN)_4(CO)(NH_3))\cdot 1.5H_2O$. Considering this composition in conjunction with that of the crude powder, the powder seems to consist of a complex anion $(Fe(CN)_4(CO)(NH_3))^{2-}$ and a complex cation $(Fe(NH_3)_3)^{2+}$.

Summary

Iron pentacarbonyl has been found to react with ammonia under high pressure of carbon monoxide at temperatures higher than 150°C, to result in a stable powder usually having the practical composition $Fe_2(CN)_4(CO)(NH_3)_4$. In a particular case of the reaction the composition tends to increase in (CO) but decrease in (NH_3), till it attains the composition $Fe_2(CN)_4(CO)_2(NH_3)_3$.

Besides this compound having a different chemical composition from those found by J. A. Müller and thereafter by W. Hieber et al., its manufacturing procedure is characterized by the use of iron pentacarbonyl and ammonia as the starting materials.

The product obtained by the reaction of iron pentacarbonyl and ammonia under high pressure of carbon monoxide has been found to accelerate markedly the formation of formamide from carbon monoxide and ammonia. The product comprises powder and brown liquor, and further the liquor consists of formamide, ammonium carbamate, urea and a minute quantity of an iron salt, among which urea seems most effective for the acceleration.

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