XXVI.—*The Chemical Reactions of Nickel Carbonyl.*
Part I. Reactions with the Halogens and other
Inorganic Substances.

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THE previous investigation of the physical properties and stability of nickel carbonyl (*Proc. Roy. Soc.*, 1903, 51, 427) having shown that the compound was much more stable than had hitherto been supposed, it was thought of interest to study its chemical reactions and stability more fully.

A few of the simpler decompositions of the compound were observed by Dr. Mond and his collaborators (*Trans.*, 1890, 57, 749), some further observations were recorded by Berthelot (*Compt. rend.*, 1891, 113, 679), and the product of oxidation in moist air has been studied by the last-mentioned chemist and by Lenher and Loos (*Amer. Chem. J.*, 1899, 22, 114).

The authors have studied a number of the reactions of the compound with the view of throwing further light on its chemical nature and structure, and its possible use as a synthetical agent. The present paper contains an account of its interactions with certain elements and simple inorganic compounds, studied mainly from a thermochemical point of view.

The heat of formation of liquid nickel carbonyl from metallic nickel and gaseous carbon monoxide, as determined by Mittasch (*Zeit. Physikal. Chem.*, 1902, 40, 49), lies between 51 and 55 Cal., the mean value being 52.17 Cal. Reicher had previously obtained the value 59.5 Cal. from the combustion of the compound. Taking the lower value and Thomsen's values for other nickel compounds, it might be expected that nickel carbonyl would be readily decomposed by chlorine or bromine, but not by iodine or sulphur, whereas it is actually decomposed completely by the four elements with the production of the corresponding nickel compounds and carbon monoxide.

In no case in which nickel carbonyl has been decomposed by elements has any combination of the carbon monoxide with the element been observed. This is remarkable since it might be expected that combination would take place more readily when the monoxide was in the so-called 'nascent' state.

Again, in the decomposition with hydrogen iodide and hydrogen sulphide, carbon monoxide is set free, and combination with hydrogen does not occur to any appreciable extent, if at all.

The Halogens and their Compounds.

The reaction with the halogens was investigated in solution in pure, dry carbon tetrachloride, the mode of procedure being briefly as follows. Standard solutions of the carbonyl derivative and the halogen were made, varying in strength from normal to decinormal, 1—10 c.c. of the carbonyl solution were introduced into a Lunge nitrometer over mercury followed successively by some tetrachloride and a very slight excess of the solution of the halogen, the mixture being then shaken and the volume of gas evolved measured after the reaction was completed. This volume was then corrected to normal temperature and pressure by comparison with another nitrometer containing a known volume of air enclosed over carbon tetrachloride, and the gas was afterwards examined to ascertain whether it was pure carbon monoxide.

Experiments were also made at low temperatures to see whether the liquid or solid halogens had any action on solid nickel carbonyl.

Chlorine.

On mixing normal solutions in carbon tetrachloride, a brisk evolution of gas takes place at once and a grey solid is precipitated. From 1 c.c. of normal nickel carbonyl solution and 1.1 c.c. of normal chlorine solution, 49.0 c.c. of gas at 16° and 755 mm. were evolved, the volume when corrected to 0° and 760 mm. being 45.2 c.c.

The volume of carbon monoxide theoretically obtainable being 44.8 c.c., it is clear that complete decomposition has taken place into carbon monoxide or a mixture of this gas and carbonyl chloride. The gas, when tested for carbonyl chloride by treatment with water or aqueous sodium carbonate, gave indications that at most only a trace of the gas was formed, even when a considerable excess of chlorine had been used.

The solid product when collected and analysed was found to be pure anhydrous nickel chloride.

The heat of the reaction $[\text{Ni}, \text{Cl}_2]$ is given by Thomsen (*Thermochemische Untersuchungen*, 3, 307) as 74.53 Cal., hence the reaction $[\text{Ni}(\text{CO})_4, \text{Cl}_2]$ should occur with the evolution of 22.36 Cal.: a considerable rise of temperature does occur during the reaction.

No action occurs in a mixture of solid chlorine and solid nickel carbonyl, but when the chlorine becomes liquid the reaction seems to begin and to proceed steadily.

Bromine.

The reaction between normal solutions in carbon tetrachloride takes place rapidly and ends almost immediately after complete mixture, as in the case of chlorine.

The gas evolved was pure carbon monoxide and the solid on analysis was found to be pure anhydrous nickel bromide.

One c.c. of nickel carbonyl solution and 1.1 c.c. of normal bromine solution gave 47.2 c.c. of gas at 12° and 758 mm. The corrected volume of the gas is 44.5, whereas theory requires 44.8 as before.

Thomsen (*loc. cit.*) gives the heat of the reaction $(\text{Ni}, \text{Br}_2, \text{aq})$ as 71.82 Cal., so that, unless the heat of hydration of nickel bromide is exceptionally great and the heat of solution exceptionally small, the reaction $[\text{Ni}(\text{CO})_4, \text{Br}_2]$ should nevertheless occur with evolution of heat, as is actually found to be the case: a distinct rise of temperature takes place during the reaction.

Solid nickel carbonyl and solid bromine did not react, and when the mixture was gradually warmed it underwent no change until the bromine became liquid, when the reaction between the solid carbonyl and the liquid bromine proceeded rapidly.

Iodine.

When a normal solution of nickel carbonyl in carbon tetrachloride was mixed with an $N/5$ or $N/10$ solution of iodine in the same solvent, a brown or black solid was deposited and carbon monoxide was slowly evolved. On examination the solid proved to be nickel iodide. The reaction between 1 c.c. of the carbonyl solution and 5 c.c. of $N/5$ iodine solution was completed in about half an hour, and the theoretical quantity of carbon monoxide was produced, as in the other cases.

Analysis of the solid, after heating at 100° , gave $Ni=18.9$. $I=80.6$. Calculated for NiI_2 , $Ni=18.9$. $I=81.1$ per cent.

Thomsen (*loc. cit.*) gives the heat of the reaction (Ni, I_2, aq) as 41.4 Cal. Now, unless the sum of the heats of hydration and solution of nickel iodide is negative, the reaction $[Ni(CO)_4, I_2]$ should be endothermic. A rough experiment was made which showed that the combined heat of solution and hydration of nickel iodide was positive, but small, being approximately 614 cal.

It was therefore important to determine whether any considerable fall of temperature occurred during the reaction. Experiments were made in which a definite volume of normal nickel carbonyl solution in different solvents was placed in a bulb, which was broken in an excess of $N/10$ iodine dissolved in the same solvent and contained in a bottle, insulated as far as possible from extraneous sources of heat. The mixture was stirred, and the change of temperature observed by means of an accurate thermometer.

A mixture of 80 c.c. of $N/5$ iodine and 8 c.c. of normal nickel carbonyl in carbon tetrachloride, was initially at 15° , and in the course of 13 minutes the temperature fell to 13.8° , the reaction being by that time nearly completed.

A mixture of 80 c.c. of $N/10$ iodine, and 7 c.c. of normal nickel carbonyl in alcohol, was initially at 15.4° , but after 23 minutes, when the reaction was practically completed, the temperature had fallen to 14.7° .

In both these cases the fall is scarcely greater than would be expected to occur by the evaporation of a quantity of the liquid necessary to saturate the carbon monoxide evolved with its vapour at the temperature of the experiment. Sufficient data are not available to calculate the expected fall of temperature accurately, but the rough estimate which can be made with the incomplete data obtainable is of the above order.

It became, therefore, interesting to ascertain the source of the energy necessary to carry out the reaction. Experiments described

below on the velocity of the evolution of the carbon monoxide show that the reaction proceeds steadily at the ordinary temperature, and is a normal bimolecular reaction, as might be expected. The energy cannot be derived from radiant light or heat, since the reaction proceeds quite as rapidly when such radiations are screened off as completely as possible.

An indication of the possible source of the energy was obtained when the reaction was carried out in ethereal solution. In this case the nickel iodide is usually first deposited as a viscid brown liquid, which then changes into a mass of large pale green, tabular crystals, but very occasionally the green crystals seem to be formed directly. These crystals, when filtered off rapidly, change to the black iodide, and give off ether in the process; they may therefore be considered as consisting of nickel iodide united with ether of crystallisation.* The loss of ether is so rapid when the crystals are taken out of the solvent, that it is quite impossible to analyse them. Somewhat similar phenomena have also been observed in other solvents, for example, in chloroform the iodide is deposited in brown, tabular crystals, which rapidly change when removed from the solution, and it is therefore probable that the nickel iodide forms molecular complexes either with the solvent or with iodine, even when there is no visible evidence of their existence, and thus gains the energy necessary to carry out the reaction. However, the tendency to form these complexes cannot be very great, since the anhydrous iodide does not combine with these solvents when mixed with them at the ordinary temperature.

This hypothesis as to the source of the energy required receives some slight support from the fact that solid iodine has scarcely any action on liquid nickel carbonyl, although this is partly due to the fact that the halogen is insoluble in the latter.

The Order of the Reaction and its Velocity in Chloroform.

On investigating the velocity of the reaction in chloroform solution by observing the rate of evolution of carbon monoxide, it was found that the reaction proceeded quite normally at the ordinary temperature and, by altering the concentration, it was found that the reaction was of the second order as might be expected from the equation $\text{Ni(CO)}_4 + \text{I}_2 = \text{NiI}_2 + 4\text{CO}$, providing that the iodine molecules are diatomic in chloroform solution. The experiments were made as simple as possible, the object being merely to see that the reaction proceeded steadily.

Three experiments are quoted and the results are shown by the appended curves, in which the ordinates represent the number of cubic

* Compare the formation of $\text{MgBr}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ and $\text{MgI}_2 \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ (*Compt. rend.*, 1901, **132**, 835) and (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 610).

centimetres of gas evolved and the abscissæ represent the time in minutes, the temperature being 12° .

Curve I, 10 c.c. $N/5$ $Ni(CO)_4$ + 30 c.c. $N/10$ iodine in 50 c.c.

„ II, 5 „ $N/5$ $Ni(CO)_4$ + 30 „ $N/10$ iodine in 50 „

„ III, 5 „ $N/5$ $Ni(CO)_4$ + 15 „ $N/10$ iodine in 50 „

It is readily seen that the evolution of gas proceeds steadily without cessation from the beginning to the time when the observations ceased.

The order of the reaction was calculated by means of the formula

$$n = \frac{\log dC_1/dt / dC_2/dt}{\log C_1/C_2}$$

for three pairs of experiments I and III, and the following three values of n were obtained, 2.03, 2.20, and 2.00, so that the reaction is evidently one of the second order.

In calculating the velocity constant, very satisfactory results cannot

be obtained, probably owing either to some lag in the evolution of the gas from the solvent or to some disturbing side reactions. The value of k , however, appears to be about 0.0005, the unit of time being a minute.

Cyanogen.

Gaseous cyanogen appears to have no action on gaseous or liquid nickel carbonyl. Cyanogen gas, enclosed in a Lunge nitrometer over mercury, when mixed with a little nickel carbonyl immediately increased in volume owing to the high vapour pressure of the carbonyl; but afterwards the volume remained constant for several days and no solid was deposited.

With an alcoholic solution of cyanogen, however, a reaction took place with moderate ease, nickel cyanide and carbon monoxide being produced. The reaction proceeded to the end, and the theoretical quantity of gas was evolved.

The heat of formation of hydrated nickel cyanide is 50.5 Cal. (Varet, *Compt. rend.*, 1896, 122, 1123), it is therefore slightly greater than that of nickel iodide, so that the reaction here, again, must be promoted by the formation of molecular complexes as in the case of the iodide.

Iodine Monochloride.

When the brown solution of iodine monochloride in chloroform is mixed with a solution of nickel carbonyl in the same solvent, a violent reaction immediately takes place, a light brown solid is precipitated, and the solution becomes purple. The rate of evolution of gas then diminishes appreciably and the purple colour of the solution gradually disappears. The gas evolved is carbon monoxide, and the solid product of the reaction is a mixture of nickel chloride and iodide.

The reaction obviously proceeds in two distinct stages according to the equations

the first stage taking place rapidly with liberation of iodine, which then reacts more slowly with a further quantity of nickel carbonyl.

Iodine Trichloride.

The reaction here proceeds exactly as in the case of the monochloride. The brown solution in chloroform or carbon tetrachloride at once becomes purple and gas is evolved very rapidly; the evolution of gas then becomes slower and the purple colour gradually disappears. The

reaction clearly occurs in two distinct stages, as in the case of the monochloride, the chloride being formed in preference to the iodide as would be expected from their respective heats of formation.

Cyanogen Iodide.

When the colourless alcoholic solution of cyanogen iodide is mixed with a similar solution of nickel carbonyl, a light drab precipitate is at once formed, carbon monoxide is evolved and the solution turns brown. The precipitate is nickel cyanide and free iodine remains in the solution. The evolution of gas continues, and a darker precipitate is produced which now consists of nickel iodide.

A chloroform solution of cyanogen iodide, which is also colourless, behaves similarly, gas is evolved and a light drab precipitate produced, the solution becoming purple and containing free iodine. The evolution of gas continues and the precipitate turns black, or, if the tube is not shaken, a black precipitate of nickel iodide settles on the top of that first formed.

Here, again, it is clear that the reaction proceeds in stages, nickel cyanide and free iodine being first formed according to the equation

and then the iodine reacts with a further quantity of nickel carbonyl to produce nickel iodide. This shows clearly that the heat of formation of nickel cyanide is greater than that of the iodide in alcoholic or chloroform solutions, just as in aqueous solution.

The Hydrides of the Halogens.

Dry hydrogen chloride or bromide, when mixed with nickel carbonyl over mercury, at once increases in volume owing to the vapour pressure of the carbonyl, the increase being exactly that amount which would be expected from the known value of the vapour pressure. Practically no further change could be observed on allowing the mixture to remain for several days. A minute amount of solid was deposited in some cases, but there was obviously no extensive reaction.

The reaction between hydrogen iodide and nickel carbonyl was investigated as follows, the use of mercury being inadmissible on account of its action on the acid gas. A glass bulb was carefully exhausted and then filled with hydrogen iodide at a slightly reduced pressure, a little nickel carbonyl was then admitted, excess being avoided at first. The gases soon reacted with the deposition of a black solid, the gaseous products were examined by passing through a U-tube immersed in liquid air and collecting the uncondensable gas and afterwards fractionating the condensed portions. The uncondensed gases

consisted of hydrogen and carbon monoxide, the condensable part being hydrogen iodide and nickel carbonyl. No formaldehyde could be detected. The solid produced was pure nickel iodide and contained no free iodine.

A solution of hydrogen iodide in chloroform reacts very rapidly with a similar solution of nickel carbonyl, producing carbon monoxide and a mixture of solids containing nickel iodide and free iodine, which has not yet been fully examined.

Sulphur.

A solution of sulphur in carbon disulphide reacts slowly with nickel carbonyl in the absence of air, evolving a gas and forming a black solid. The gas evolved is not immediately absorbed by an alcoholic potash solution and therefore contains no carbon oxysulphide, it is, however, taken up by a solution of cuprous chloride in hydrochloric acid and is therefore practically pure carbon monoxide. The solid contains nickel and sulphur. A similar reaction occurs with a solution of sulphur in xylene, but in both cases it takes place very slowly.

With 1.5 c.c. of a normal solution of nickel carbonyl and an excess of a solution of sulphur in carbon disulphide, gas was steadily evolved for four days until about 78 c.c. had been collected, this being approximately the amount to be expected.

The heat of the reaction $(\text{Ni}_2\text{S}_3, n\text{H}_2\text{O})$ is given by Thomsen (*loc. cit.*) as 19.4 Cal., so that the reaction $[\text{Ni}(\text{CO})_4, \text{S}]$ might therefore be strongly endothermic. However, there is no marked fall of temperature during the reaction, no energy can be obtained from radiant light since the black deposit rapidly renders the walls of the vessel quite opaque, and moreover, the reaction proceeds in the dark. The solid, on examination, was found to be a higher sulphide than NiS , having, in fact, a composition closely corresponding to Ni_2S_3 . Found $\text{Ni} = 54.8$. Ni_2S_3 requires $\text{Ni} = 54.5$ per cent. Hence the necessary energy may be derived from the formation of this more complex compound.

Hydrogen Sulphide.

Hydrogen sulphide mixed with excess of nickel carbonyl reacts very slowly, depositing a black solid and liberating hydrogen and carbon monoxide. In about a week only about 40 per cent. of the sulphide had reacted.

In alcoholic solution, the reaction proceeds more quickly, and the black precipitate first formed acquires a bronze lustre. On analysis, this solid proved to be the monosulphide, NiS . Found $\text{Ni} = 64.4$. NiS requires $\text{Ni} = 64.7$ per cent.

The gases evolved contained hydrogen and carbon monoxide, and no formaldehyde could be identified with certainty among the products of reaction.

Sulphuric Acid.

Berthelot (*Compt. rend.*, 1891, 112, 1343) states that nickel carbonyl in contact with concentrated sulphuric acid detonates after a few minutes. This is quite contrary to our experience, for even when slightly moist nickel carbonyl was used, the reaction always took place slowly without any great evolution of heat.

Some nickel carbonyl and sulphuric acid were sealed up in a tube, a reaction went on very slowly during several weeks. The tube was opened from time to time and examined. Considerable pressure was developed and a yellow precipitate was formed. The gas evolved was a mixture of carbon monoxide and hydrogen, a little hydrogen sulphide was observed later, and the yellow solid proved to be nickel sulphate, so that the reaction seems to proceed according to the equation :

Phosphorus.

Nickel carbonyl, when mixed with a solution of phosphorus in carbon disulphide and left out of contact with air, undergoes no change after several weeks. If, however, dry air has access to the mixture, a reaction slowly occurs with the evolution of gas and the formation of a black solid which contains nickel and phosphorus, but which has not yet been fully examined.

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