

### 377. *Phosphides of Nickel: The Reaction between Phosphorus and Nickel Carbonyl.*

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WHILE investigating the effect of certain non-metals and their compounds on the rate of formation of nickel carbonyl from carbon monoxide and nickel-containing materials, it was observed that a black mirror-like deposit containing nickel and phosphorus slowly formed on the walls of the reaction vessel when carbon monoxide charged with phosphorus vapour was led over reduced nickel at  $50^{\circ}$ . The novel conditions of formation of the deposit led us to inquire into the mode of its formation and its chemical composition. We have found that it is *nickel monophosphide*,  $\text{NiP}$ , and that it is also formed by the interaction at  $50^{\circ}$  of phosphorus and nickel carbonyl in the vapour state. Berthelot (*Compt. rend.*, 1891, **112**, 1347) noted the production of a black shiny deposit under similar conditions, but did not investigate the substance.

A black, amorphous, relatively unstable powder, probably containing *nickel tetraphosphide*,  $\text{NiP}_4$ , is precipitated when nickel carbonyl vapour is bubbled through an excess of liquid phosphorus or through a solution of phosphorus in turpentine.

*Phosphides of Nickel.*—Numerous phosphides of nickel have been described, *viz.*,  $\text{Ni}_3\text{P}$ ,  $\text{Ni}_5\text{P}_2$ ,  $\text{Ni}_2\text{P}$ ,  $\text{Ni}_3\text{P}_2$ ,  $\text{Ni}_2\text{P}_3$ ,  $\text{NiP}_2$ ,  $\text{NiP}_3$ , all prepared by thermal methods, and  $\text{Ni}_5\text{P}_2$ ,  $\text{Ni}_2\text{P}$  also by precipitation methods.  $\text{Ni}_5\text{P}_2$ ,  $\text{Ni}_2\text{P}$ , and  $\text{Ni}_2\text{P}_3$  have been prepared by direct union of the two elements at red heat in an inert atmosphere (Pelletier; Davy, *Phil. Trans.*, 1808, **98**, 333; and Granger, *Compt. rend.*, 1896, **122**, 1484). Phosphides are also formed by reaction between phosphorus halides or phosphine with nickel at high temperatures (Granger, *Ann. Chim. Phys.*, 1898, **14**, 49). The existence of  $\text{Ni}_3\text{P}$ ,  $\text{Ni}_5\text{P}_2$ , and  $\text{Ni}_2\text{P}$  has been demonstrated by Konstantinoff (*Z. anorg. Chem.*, 1908, **60**, 405) from a study of the freezing point curves of alloys of the two elements.

In all the thermal methods, grey, crystalline, stable phosphides are formed, which, although soluble in nitric acid, are almost unaffected by non-oxidising acids. The nickel phosphides obtained

by precipitation methods, however, are amorphous black powders and are readily oxidised.

Schenck (J., 1874, 27, 214) obtained a black modification of  $\text{Ni}_2\text{P}$  by heating an alkaline solution of nickel tartrate with phosphorus; and Kulisch (*Annalen*, 1885, 231, 357), by passing  $\text{PH}_3$  into ammoniacal nickel salt solution, obtained a mixture of nickel and nickel phosphide. Recently, however, Scholder and Heckel (*Z. anorg. Chem.*, 1931, 198, 329) have separated fairly pure  $\text{Ni}_5\text{P}_2$  and  $\text{Ni}_2\text{P}$  from the mixture of phosphides precipitated from acid solutions of nickel salts by alkaline hypophosphite solutions.

#### EXPERIMENTAL.

A. *Nickel Monophosphide*.—CO, charged with the vapours of P and  $\text{Ni}(\text{CO})_4$ , was passed through a glass tube which was gradually heated. Reaction occurred at about  $50^\circ$ , with formation of a black shiny deposit; this was removed under  $\text{H}_2\text{O}$ , washed with EtOH, then with  $\text{Et}_2\text{O}$ , and any free P extracted with  $\text{CS}_2$ .

No reaction occurred when CO containing P vapour or when  $\text{PH}_3$  was bubbled through liquid  $\text{Ni}(\text{CO})_4$ , but a similar deposit to the above was formed by reaction of  $\text{Ni}(\text{CO})_4$  vapour with  $\text{PH}_3$ .

When  $\text{Ni}(\text{CO})_4$  vapour was bubbled through liquid P at  $60^\circ$ , there was obtained a mixture of (1) shiny metallic particles, and (2) black amorphous powder, which were separated by flotation, purified as above, dried in an atm. of  $\text{CO}_2$  at  $80^\circ$ , and analysed. The results were :

	Ni, %.	P, %.	Ni + P, %.	Atomic ratio, Ni : P.
(a) .....	63.12	33.94	97.06	1 : 1.02
(b) .....	64.24	34.32	98.56	1 : 1.01
(c) .....	64.06	33.80	97.86	1 : 1.00
(d) .....	62.50	34.85	97.35	1 : 1.05

The analyses refer to different preparations: (a), (b), and (c) were obtained by interaction of P and  $\text{Ni}(\text{CO})_4$  vapours, independently introduced by means of CO into the reaction tube, whereas (d) refers to the metallic deposit mechanically separated from the amorphous ppt. In the last case, the ratio P : Ni is slightly higher than in the others, but the sample probably contained traces of the black amorphous ppt. formed in the liquid P, which contains higher proportions of P (see p. 2545).

Scholder and Heckel (*loc. cit.*) showed that O and  $\text{H}_2\text{O}$  were tenaciously retained by their  $\text{Ni}_5\text{P}_2$  and  $\text{Ni}_2\text{P}$ , and their analyses showed only 96—98% of Ni + P. Slight oxidation probably accounts for the deficiency of 1.5—3% in our analyses.

Since the concn. of the reactants differed in each of the above expts., no precautions having been taken to maintain a constant flow of CO, the constancy of the ratio Ni : P establishes the existence of the compound  $\text{NiP}$ .

*Properties of Nickel Monophosphide*.—The phosphide consists of black, non-magnetic, metallic scales, which were seen under the microscope to possess a fine cryst. structure. On being heated in air, it loses P, and  $\text{Ni}_3(\text{PO}_4)_2$  remains. The phosphide is scarcely attacked by HCl, but is easily

sol. in  $\text{HNO}_3$  and in aqua regia. It is not spontaneously inflammable in air, nor ignited by fuming  $\text{HNO}_3$ . Although prep. at a temp. of only  $50^\circ$ , NiP has properties compatible with its inclusion in the class of phosphides produced by thermal means (see p. 2543).

B. *A Higher Phosphide of Nickel*.—When the amorphous powder (2) (p. 2544) was treated with  $\text{HNO}_3$ , a yellow substance was suddenly thrown out of solution; it momentarily floated on the surface before it was finally dissolved. The  $\text{HNO}_3$  in the absorption bulb, which was connected to the apparatus to trap any volatile Ni or P compound, assumed a green colour, which became yellow on standing. No Ni was found in this acid solution, so the green colour was probably due to oxides of N evolved in the reaction. P, however, was always found in the liquid in the absorption bulb when product (2) was being dissolved, whereas when the cryst. NiP was treated with  $\text{HNO}_3$ , no P escaped oxidation in the main solution.

In the following table, the first two analyses are of preps. which had been spoiled by drying under reduced press., thereby undergoing some oxidation with evolution of white fumes of oxides of P. Further preparations were dried in an atm. of  $\text{CO}_2$ .

Ni, %.	P, %.	Ni + P, %.	Atomic ratio,
			Ni : P.
39.56	35.60	75.16	1 : 1.7
35.49	45.66	81.15	1 : 2.43
32.15	67.70	99.85	1 : 3.98
31.90	68.16	100.06	1 : 4.04

The analyses of the pure product (Ni + P = 100.06%) indicate the formation of a higher phosphide, probably the *tetraphosphide*.

An attempt was made, by dilution with cold  $\text{H}_2\text{O}$ , to isolate the yellow substance mentioned above. It was repeatedly washed with cold  $\text{H}_2\text{O}$ , then with EtOH and  $\text{Et}_2\text{O}$ , and dried in a vac. desiccator over conc.  $\text{H}_2\text{SO}_4$ . The product was free from Ni and in appearance and behaviour resembled solid hydrogen diphosphide (Stock, Böttger, and Lenger, *Ber.*, 1909, **42**, 2839; Jolibois, *Compt. rend.*, 1908, **147**, 801).

*Properties of the Amorphous Nickel Phosphide*.—The amorphous preparation ignites when heated in air to about  $80^\circ$ , evolving oxides of P; when treated with fuming  $\text{HNO}_3$  it also inflames. KOH aq. and  $\text{NH}_3$  aq. readily react with this substance, evolving  $\text{PH}_3$  and H; when mixed with  $\text{KClO}_3$  and struck, it detonates violently. The above properties are very similar to those of hydrogen diphosphide, and its formation by decomp. of the amorphous nickel phosphide is consistent with the formula  $\text{NiP}_4$  for the latter.

C. *Precipitation of Phosphides of Nickel from Solutions of Phosphorus*.— $\text{CS}_2$ , although an excellent solvent for P, cannot be employed for the pptn. of phosphides of Ni since it reacts with  $\text{Ni}(\text{CO})_4$  to form NiS (Dewar and Jones, 1910, **97**, 1226). A mixture of liquid  $\text{Ni}(\text{CO})_4$  and  $\text{C}_6\text{H}_6$  containing thiophen soon darkened owing to the formation of NiS, but turpentine was unaffected by  $\text{Ni}(\text{CO})_4$ , so it was used as a solvent for P, the vapour of  $\text{Ni}(\text{CO})_4$  being bubbled through a 2% solution, which was gradually heated. Darkening occurred at about  $70^\circ$ , and a black powder was pptd. This was filtered off in an atm. of  $\text{CO}_2$ , washed with  $\text{CS}_2$ , then with  $\text{Et}_2\text{O}$ , sucked dry at the pump, and analysed in the moist state to obtain the ratio Ni : P. Another prepn. was dried in an atm. of  $\text{CO}_2$  at  $80^\circ$ , and analysed :

Sample.	Ni, %.	P, %.	Ni + P, %.	Atomic ratio,
				Ni : P.
Moist .....	11.96	27.35	—	1 : 4.38
Dry .....	32.75	55.08	87.83	1 : 3.10

The ratio P : Ni in the moist sample is somewhat higher than 4 : 1, but in the dry sample it is only 3 : 1. The total of Ni + P in the latter analysis is very low, but during the drying there was indication of some oxidation, with loss of P. There is, of course, the possibility that the prepn. is a mixture of phosphides of Ni, but if so, one phosphide would contain more P than NiP<sub>4</sub>, and it would be so unstable as to render the separation from it of chemically pure nickel phosphides very difficult.

The properties of the product (C) are similar to those of the amorphous phosphide described in (B), solid hydrogen phosphide being obtained from it by treatment with HNO<sub>3</sub>. Colson (*Compt. rend.*, 1908, **146**, 71, 401) observed the formation of the solid hydrogen diphosphide when a solution of P in turpentine was heated to 250°: in the presence of Ni(CO)<sub>4</sub>, therefore, it is possible that NiP<sub>4</sub> is pptd. on warming, but this product is not regarded as pure NiP<sub>4</sub>.

It is probable that the formation of the nickel phosphides described is due initially to a slight dissociation of Ni(CO)<sub>4</sub> into CO and highly active Ni (Dewar, *Phil. Trans.*, 1903, **427**, 71), the latter reacting with the P. In the absence of P, both as liquid and vapour, no visible mirror of metallic Ni was obtained under the same conditions of experiment, and it is probable, therefore, that P catalytically lowers the dissociation temp. of Ni(CO)<sub>4</sub>.

### Summary.

Although liquid nickel carbonyl (*i.e.*, at temperatures below 43°) does not react with phosphorus or with phosphine, interaction occurs in the vapour state even at 50°, with the formation of nickel monophosphide, a black, metallic, crystalline compound similar to the nickel phosphides produced thermally. The amorphous preparations obtained by the action of nickel carbonyl vapour on liquid phosphorus, also on a solution of phosphorus in turpentine, belong to the second class of nickel phosphides, *i.e.*, those formed by precipitation. The existence of a higher phosphide of nickel, probably NiP<sub>4</sub>, is indicated, and is supported by its relation to hydrogen diphosphide.

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