Reduction of WO_3 by Phosphorus*

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The reduction of WO_3 by elemental phosphorus at 800 °C leads to the formation of several products. Depending on the molar ratio $n(P):n(WO_3)$ in the course of this investigation, WP, WP_2, WPO_5 and, for the first time, tungsten(IV) diphosphate, WP_2O_7, were prepared. By chemical vapour transport reactions (transport agent iodine; 200 mg per ampoule; 1050→950 °C), the phosphides and phosphates of tungsten can be purified and crystallized. Heterogeneous and homogeneous equilibria, responsible for the vapour-phase transport of the tungsten compounds, will be discussed.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

Recently Martin[2] described the preparation of transition-metal phosphides by reduction of the corresponding metal oxides by aluminium in the presence of phosphorus. From the mixture of the reaction products (Al_2O_3 and the metal phosphides), the phosphides were seperated using chemical vapour transport reactions.[3] With this method[2] well formed crystals of the transition-metal phosphides were obtained. The purpose of the present paper is to examine the synthesis of transition-metal phosphides from oxides without aluminium, using an excess of phosphorus as reducing agent. Continuing the investigations of Glaum and Gruehn[4] and Kaiser,[5] dealing with phase equilibria and chemical transport experiments in metal/phosphorus/oxygen systems (metal: Ti, V, Nb), we tried to synthesize and crystallize tungsten phosphates (especially WPO_5 and WP_2O_7) starting from WO_3 and P. The structure of WPO_5 has been solved by Wang and Lii.[6] The compound is a member of the monophosphate tungsten bronze series[7] $(WO_3)_{2m}(PO_2)_4$ (m=2). Formally WP_2O_7 is also a member of this series (m=1; $W_2P_4O_{14}$), but its structure is different from those of the bronzes. To our knowledge WP_2O_7 has not been prepared before.

In addition, we tried to obtain information about the heterogenous and homogenous equilibria that are responsible for the chemical vapour transport of tungsten phosphides and phosphates.

Experimental

As starting materials, WO_3 (Fluka, > 99.9 % puriss.) and red phosphorus (Hoechst AG, Knapsack, electronic grade) were used without further purification. To reduce their

Table 1. Equilibrium experiments in the system P/WO_3.[a]

No.	Starting materials		Molar ratio, $n(P)/n(WO_3)$	Solids obtained
	P/mg	WO_3/mg		
P1	29.1	232.1	0.9386	WP, WPO_5[b]
P2	31.2	232.2	1.0059	WP, WPO_5[b]
P3	32.9	232.0	1.0617	WP, WPO_5,[b] WP_2O_7[c]
P4	34.9	232.1	1.1257	WP, WPO_5,[b] WP_2O_7
P5	43.6	231.9	1.4075	WP, WPO_5,[b] WP_2O_7
P6	45.9	231.9	1.4818	WP, WP_2O_7, WP_2[c]
P7	48.2	231.8	1.5566	WP, WP_2O_7, WP_2
P8	61.1	232.0	1.9717	WP, WP_2O_7, WP_2
P9	63.9	231.9	2.0629	WP,[c] WP_2O_7, WP_2
P10	66.8	232.0	2.1556	WP_2O_7, WP_2
P11	69.8	232.0	2.2524	WP_2O_7, WP_2
P12	89.9	231.9	2.9022	WP_2O_7, WP_2
P13	93.6	232.0	3.0205	WP_2O_7,[c] WP_2
P14	97.3	231.9	3.1412	WP_2O_7,[c] WP_2
P15	101.5	232.6	3.2669	WP_2O_7,[c] WP_2
P16	105.6	231.9	3.4091	WP_2
P17	109.8	231.9	3.5447	WP_2

[a]Usual conditions: $V \approx 7$ cm^3; iodine ≈ 50 mg per ampoule. [b]At 800 °C we obtained a black amorphous solid. Heat treatment of the isolated product at 1100 °C in evacuated silica ampoules led to chestnut-brown crystals of WPO_5. [c]Only a weak X-ray pattern was obtained.

* This is Part V of a series from our group dealing with the behaviour of anhydrous phosphates: for Part IV see Ref. 1.

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Table 2. Deposition of various tungsten phosphides and phosphates in a temperature gradient; representative experiments.[a]

Starting materials/mg			Molar ratio, $n(P)/n(WO_3$ or W)	Transport agent /mg cm^{-3}	Temperature gradient/°C, $T_2 \rightarrow T_1$	Time/h	Compounds obtained/mg	
P	WO_3	W					Source region	Sink region
31.4	232.4		1.012	8.44	950 → 900	153	–	WP (82.7) WPO_5 (176.4)
65.1	344.5		1.415	5.03	1000 → 900		WP	WP, WPO_5, WP_2O_7
61.8	233.0		1.986	8.74	1000 → 900	129	–	WP (171.5) WP_2O_7 (62.0)
99.1	232.0		3.198	8.71	950 → 850	96	β-WP_2	β-WP_2 (249.1)
123.2	230.7		3.998	8.40	1000 → 900	168	β-WP_2	β-WP_2 (153.1)
124.2		366.3	2.013	17.11	1000 → 900	98	β-WP_2	β-WP_2 (30.0)
141.4		278.3	3.016	17.20	1000 → 900	98	β-WP_2	β-WP_2 (8.5)

[a]Usual conditions: $V \approx 12$ cm^3; iodine = 100–200 mg per ampoule.

water content,[8] the empty silica ampoules ($l \approx 9$ cm; $d \approx 1.3$ cm; $V \approx 12$ cm^3) were heated (4 h; 800 °C) under vacuum ($p < 5 \times 10^{-3}$ Torr) before filling and sealing. About 50 mg iodine (Merck, > 99.5 % p.a.) were added as mineralisator in equilibrium experiments, which were carried out isothermally at 800 °C. For transport experiments with a temperature gradient applied to the ampoule, larger amounts of I_2 (100–200 mg per ampoule) were used. Detailed information on the experimental parameters of the two sets of experiments is given in Tables 1 and 2.

The transport reactions were carried out in two-zone horizontal tube furnaces, controlled by Pt–Pt/Rh thermoelements. To prevent explosions caused by over-high P_4 pressure at the beginning of the experiments, stepwise temperature increments were necessary (500 °C, 12 h; 800 °C, 12 h).

Some transport experiments were performed on a special thermobalance (a transport balance) which allows one to observe transport effects continuously during the experiments.[9] Thus, a direct determination of the deposition rate and of the deposition sequence of two or more solids is possible.

After heating, the ampoules were removed from the furnace in a way that led to condensation of the equilibrium gas phase at one end. In transport experiments, the gas phase was condensed at the source region to avoid contamination of the crystals grown in the sink. After the ampoules had been opened, the solids from the source and the sink regions were washed with dilute NaOH, H_2O and acetone, and dried at 100 °C. The phases obtained were identified by their X-ray powder pattern using the Guinier technique, with Cu $K\alpha_1$ radiation, a quartz monochromator and α-quartz as internal standard.

Results and discussion

Evaluating the results of the equilibrium experiments performed at 800 °C, we found that the reduction of WO_3 by P_4(g) leds to several mixtures of reaction products. The equilibrium solids occurring at different $n(P):n(WO_3)$ ratios are shown in Fig. 1. Only WP_2 can be obtained as a single solid phase, reducing WO_3. For this purpose, high amounts of P_4 [$n(P):n(WO_3) \geq 3.40$] were used. Starting mixtures of lower phosphorus contents lead to double or triple phase mixtures of WPO_5, WP_2O_7, WP and WP_2. In accordance with Fig. 1, the experimental results (Table 1) can be rationalized by eqns. (1)–(4), which determine the equilibrium solids with idealized $n(P):n(WO_3)$ ratios.

$$5\ WO_3(s) + 5/4\ P_4(g) = 3\ WPO_5(s) + 2\ WP(s) \quad (1)$$

$$n(P)/n(WO_3) = 1:1$$

$$7\ WO_3(s) + 10/4\ P_4(g) = 3\ WP_2O_7(s) + 4\ WP(s) \quad (2)$$

$$n(P)/n(WO_3) = 1:1.43$$

$$7\ WO_3(s) + 14/4\ P_4(g) = 3\ WP_2O_7(s) + 4\ WP_2(s) \quad (3)$$

$$n(P)/n(WO_3) = 1:2$$

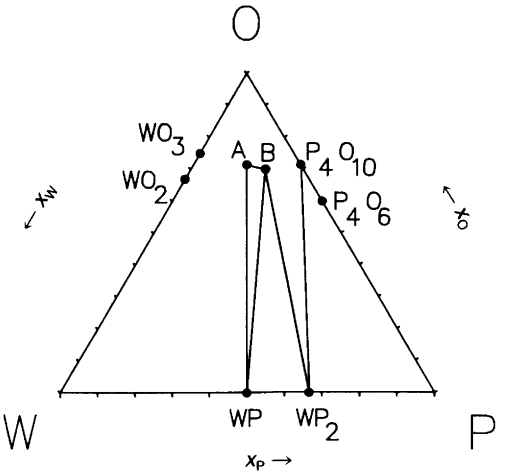

Fig. 1. Tentative phase diagram of the system W/P/O at 800 °C. Intermediate phases WO_y(y = 2.72; 2.92) are omitted. The representation of x_i is given as a percentage. (A) WPO_5; (B) WP_2O_7.

$$10\ WO_3(s) + 8\ P_4(g) = 10\ WP_2(s) + 3\ P_4O_{10}(g) \quad (4)$$

$$n(P)/n(WO_3) = 1{:}3.2$$

Note that, at higher temperatures of the transport experiments (1000 °C) in the system W/P/O, no $WP_2(s)$ has been obtained. Obviously, at 800 °C, a small excess of phosphorus is sufficient to stabilize $WP_2(s)$, whereas under the conditions of the transport experiments, higher amounts of additional phosphorus are necessary to avoid decomposition of $WP_2(s)$ according to eqn. (5).

$$WP_2(s) = WP(s) + 1/4\ P_4(g) \quad (5)$$

Under these conditions, the equilibrium gas phase cannot only contain $P_4O_{10}(g)$ alone, but must consist of a mixture of $P_4O_{10}(g)$, $P_4(g)$ and various intermediate phosphorus oxides [$P_4O_n(g)$; n = 6–9]. Unfortunately, these oxides are not well characterized from the thermochemical point of view, and therefore no quantitative evaluation of the various partial pressures is possible. The lack of well-determined thermodynamic data for the intermediate phosphorus oxides also prevents a complete calculation of the equilibrium gas-phase composition over tungsten phosphide/tungsten phosphate solids, under the influence of iodine as transport agent. Nevertheless, the method of chemical vapour transport[4] is a useful tool for the purification and crystallization of tungsten phosphides (WP, WP_2) and tungsten phosphates (WPO_5, WP_2O_7), as can be seen from the experiments outlined in Table 2. Using iodine as transport agent (ca. 200 mg I_2 per ampoule), WP and WP_2, as well as WPO_5 and WP_2O_7, migrate in a temperature gradient from the upper temperature region to the lower one.

Thus, WP (MnP-type)[10] and WP_2 were obtained in well formed crystals which show metallic lustre. For WP_2 two modifications are known.[11] In our experiments we always obtained the β-form, which is isotypic to molybdenum diphosphide. This observation is in agreement with a given transition temperature below 800 °C.[11] While the phosphides do not adhere to the walls of the silica ampoules and can be removed easily, the phosphates WPO_5 (chestnut-brown crystals) and WP_2O_7 (black cubelets) have to be loosened from the walls by treatment with dilute HF. Despite this observation, no attack on the walls of the silica ampoules, caused by interaction of SiO_2 with the equilibrium gas phase, has been observed during the transport experiments.

The deposition rate of tungsten phosphides and phosphates has been observed to be 0.5–5 mg h^{-1}. As can be seen from the experiments, the migration of WP and WP_2 (transport agent I_2; $T_2 \rightarrow T_1$) in the absence of oxygen (preparation of the phosphides from the elements) is very slow and can be increased by adding small amounts of WO_3 or H_2O. Experiments carried out on a transport balance[9] indicate that from an equilibrium solid (1050 °C) consisting of WP and WPO_5, first a mixture of both compounds is

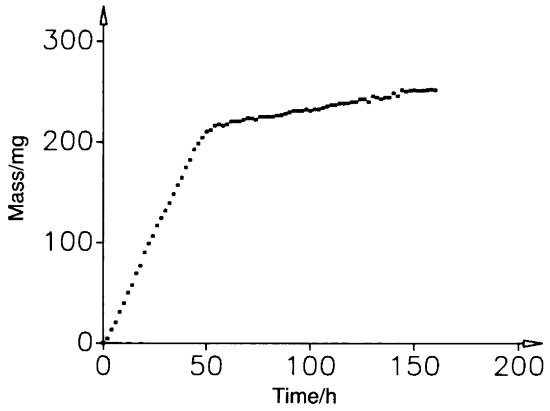

Fig. 2. Mass *vs.* time diagram of a transport experiment on the transport balance for a molar ratio $n(P)$: $n(WO_3)$ = 1:1. The temperature gradient is 950 → 900 °C; iodine = 8.44 mg cm^{-3}. The first period, 0–53 h, corresponds to the simultaneous deposition of WP and WPO_5. The second period, 53–153 h, corresponds to the deposition of WP alone.

removed to the zone of lower temperature (950 °C) under the influence of iodine as transport agent. After the complete deposition of the phosphate (as a WP–WPO_5 mixture) in the sink region, the remaining WP is transported with a lower rate, as can be seen from a representative diagram describing the mass deposition at the sink as a function of time (Fig. 2). Although a complete thermodynamic description of the observed chemical transport phenomena can not be given, the experimental results, together with observations[12] made on chemical transport reactions on tungsten oxides, lead to some ideas how the chemical vapour transport of tungsten phosphides and phosphates might occur. From the investigations of Schäfer *et al.*[13] we know that in the presence of iodine and oxygen, $WO_2I_2(g)$ is the most important tungsten carrier. Other tungsten iodides or tungsten oxide iodides can be neglected as being responsible for the chemical vapour transport of tungsten compounds. Under the influence of small amounts of water one might assume equations such as eqn. (6) and (7) to be the most important equilibria for vapour-phase transport of WP and WP_2, according to the chemical transport of WS_2.[13]

$$WP(s) + 2\ H_2O(g) + I_2(g) =$$

$$WO_2I_2(g) + 1/4\ P_4(g) + 2\ H_2(g) \quad (6)$$

$$WP_2(s) + 2\ H_2O(g) + I_2(g) =$$

$$WO_2I_2(g) + 1/2\ P_4(g) + 2\ H_2(g) \quad (7)$$

The simultaneous transport of WP and WPO_5 implies that equilibria such as eqn. (8) may play a major part in chemical transport reactions with tungsten phosphates.

$$14/5\ WPO_5(s) + 9/5\ WP(s) + 4\ I_2(g) =$$

$$4\ WO_2I_2(g) + P_4O_6(g) \quad (8)$$

Table 3. X-Ray powder pattern (λ = 1.54051 Å) of WP_2O_7.

h	*k*	*l*	$4\theta_{obs}$/°	$4\theta_{calc}$/°	I_{obs}[a]	I_{calc}	*d*/Å
1	1	1	38.638	38.596	vs	742.4	4.5955
2	0	0	44.657	44.638	vs	1000.0	3.9798
2	1	0	50.029	49.987	w	168.8	3.5597
2	1	1	54.814	54.874	w	152.6	3.2495
2	2	0	63.606	63.540	s	468.0	2.8142
2	2	1		67.506	–	1.3	2.6532
3	1	1	74.912	74.881	s	607.1	2.3999
2	2	2	78.262	78.344	w	154.2	2.2978
3	2	1		84.912	–	1.0	2.1273
4	0	0	91.107	91.019	vw	73.3	1.9899
4	1	0		94.061	–	26.4	1.9305
3	2	2		94.061	–	10.9	1.9305
4	1	1		96.960	–	19.7	1.8761
3	3	1	99.784	99.796	m	212.0	1.8261
4	2	0	102.577	102.573	m	160.7	1.7798
2	4	0	102.577	102.573	m	215.7	1.7798

[a]vs: very strong; s: strong; m: medium; w: weak; vw: very weak.

Schäfer mentioned the occurrence of SO_2(g) in the equilibrium gas phase for chemical transport reactions of WS_2 with I_2. For the same reasons, phosphorus oxides should be present in the gas phase over mixtures of tungsten phosphides and tungsten phosphates and iodine. WP_2O_7, which to our knowledge has not been prepared before, belongs to the large family of isotypic tetravalent metal disphosphates MP_2O_7 (M = Si, Ti, Zr, Sn, Hf, Mo, Re, Th, U).[14–17] It has been identified by a comparisation of its X-ray powder pattern with the pattern calculated (using the program Lazy Pulverix)[18] for MoP_2O_7 using the crystallographic data given in Ref. 19. The evaluation of the powder pattern (Table 3) leads to a cubic unit cell with a = 7.9597(12) Å. As observed for most of the abovementioned diphosphates, WP_2O_7 seems to crystallize in a cubic supercell 27 times the volume of the small subcell. All weak reflections of the X-ray powder pattern which are not explained by the small unit cell can be indexed assuming a lattice constant $a' = 3a$.

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