# Reduction of Sodium Cyclotriphosphate by Metallic Molybdenum

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**Abstract**—The products of the reaction between sodium cyclotriphosphate and powder Mo in vacuum at temperatures up to 1000°C were characterized by x-ray diffraction and <sup>31</sup>P nuclear magnetic resonance. Above 650–700°C, the reaction yields MoP and amorphous sodium phosphates (orthophosphate, pyrophosphate, and cyclotetraphosphate) containing Mo in the oxidation state 5+. At the Mo content ensuring the largest percentage of sodium cyclotetraphosphate in the reaction products, these also contain a small amount of elemental phosphorus.

## INTRODUCTION

Transition-metal phosphides find many engineering applications. Most of these compounds can be prepared by reacting elemental mixtures [1, 2]. At the same time, there are other routes [3], in particular, reduction of phosphates by metals [4–6]. In this paper, we examine the possibility of preparing molybdenum phosphide via reduction of sodium polyphosphate by metallic molybdenum.

### **EXPERIMENTAL**

As starting reagents, we used sodium cyclotriphosphate,  $Na_3P_3O_9$ , prepared by the thermal dehydration of monobasic sodium phosphate,  $NaH_2PO_4$ , and powder Mo prepared via hydrogen reduction of molybdenum trioxide [7]. All of the chemicals were of analytical grade.

Mixtures of Na<sub>3</sub>P<sub>3</sub>O<sub>9</sub> and Mo metal were reacted by heating in evacuated 6-cm<sup>3</sup> quartz tubes, followed by air cooling. The reaction products were analyzed chemically and characterized by x-ray diffraction (XRD) on a DRON-0.5 powder diffractometer (Cu $K_{\alpha}$  radiation) and liquid-phase <sup>31</sup>P nuclear magnetic resonance (NMR) on a WP-80 spectrometer. Samples for NMR measurements were prepared by grinding and mixing with an aqueous suspension of the H-form of the DOWEX ion-exchange resin for 24 h. After filtration, the contents of various phosphates in the filtrate were determined by NMR.

# **RESULTS AND DISCUSSION**

Up to 600–650°C, no reaction between  $Na_3P_3O_9$  and Mo took place, despite the melting of the salt. Accord-

ing to XRD data, the only crystalline phase in the mixtures heated to these temperatures was Mo metal. No XRD peaks characteristic of sodium phosphates were observed, presumably because  $Na_3P_3O_9$  converted into a high-molecular linear polymer, having a tendency to vitrify.

After heating a mixture of  $Na_3P_3O_9$  and 20 mol % Mo to just above 650°C, the XRD pattern contained



Fig. 1. Intensity ratio of the major XRD peaks from MoP and Mo as a function of (a) reaction temperature and (b) Mo content.



Fig. 2. Percentages of phosphorus present as (1) sodium orthophosphate, (2) sodium pyrophosphate, and (3) sodium cyclotetraphosphate in the products of the reaction between  $Na_3P_3O_9$  and different amounts of Mo at 1000°C for 30 min.



Fig. 3. Percentages of phosphorus present as (1) sodium orthophosphate, (2) sodium pyrophosphate, and (3) sodium cyclotetraphosphate in the products of the reaction between  $Na_3P_3O_9$  and 20 mol % Mo at 1000°C for various lengths of time.



Fig. 4. Percentages of phosphorus present as (1) sodium orthophosphate, (2) sodium pyrophosphate, and (3) sodium cyclotetraphosphate in the products of the reaction between  $Na_3P_3O_9$  and 20 mol % Mo at different temperatures for 30 min.

weak diffraction peaks from MoP. The intensity of these peaks was found to rise with increasing reaction temperature (Fig. 1a), while the peaks from Mo became progressively weaker. The XRD pattern of the 1000°C reaction products was dominated by the reflections from MoP. After reaction at 1100°C, only peaks from MoP were observed.

As would be expected, the phase composition of the reaction products was strongly dependent on the starting mixture composition. The reaction of  $Na_3P_3O_9$  with 20 mol % Mo at 1000°C yielded MoP and unreacted Mo, whereas at a lower Mo content, MoP was the only crystalline phase formed (Fig. 1b). As the percentage of Mo in the starting mixture was raised, the amount of unreacted Mo in the reaction products increased.

The reaction rate was found to be fairly fast: at 1000°C, most of the Mo in a mixture of  $Na_3P_3O_9$  and 20 mol % Mo converts into MoP in just 5 min. Subsequently, the percentages of Mo and MoP change little.

Yet another reaction product is elemental phosphorus, which deposits on the tube wall in the course of the reaction in mixtures containing  $30-50 \mod \%$  Mo. At lower Mo contents, no elemental phosphorus was formed.

The formation of MoP and elemental phosphorus implies phosphorus deficiency in the starting salt and, hence, its depolymerization. <sup>31</sup>P NMR results confirm that, in mixtures containing 20 mol % Mo, about 50% of the phosphorus not incorporated in MoP is present as sodium pyrophosphate and about 15% as sodium orthophosphate (Fig. 2). The rest of the phosphorus is incorporated in sodium cyclotetraphosphate. With increasing Mo content, the percentage of sodium cyclotetrawhile of phosphate increases. that sodium pyrophosphate decreases slightly. As the Mo content becomes higher than 40 mol %, the percentage of sodium cyclotetraphosphate begins to decrease, and that of sodium pyrophosphate rises. The highest pyrophosphate content and the lowest cyclotetraphosphate content were obtained by reacting Na<sub>3</sub>P<sub>3</sub>O<sub>9</sub> with 60-70 mol % Mo.

The kinetic curves plotted using NMR results demonstrate that sodium cyclotetraphosphate is an intermediate reaction product (Fig. 3). From the data displayed in Fig. 4, it follows that sodium cyclotetraphosphate forms mainly in the temperature range 700–800°C, where the reaction rate is fairly slow.

Four-membered rings are atypical of sodium phosphates but are common in phosphates of some multivalent metals [8]. It seems likely that the rings comprising four PO<sub>4</sub> tetrahedra result from the presence of highvalency Mo ions, which link the starting polymer after an appropriate rearrangement at high temperatures. This is possible if the oxidized molybdenum is incorporated not only in MoP but also in amorphous phosphates. When dissolved in an acid, the reaction products turn deep blue, characteristic of molybdenum blue. Therefore, the molybdenum in the reaction products is likely to be mainly in the oxidation state 5+.

The major reaction in a mixture of sodium cyclotetraphosphate and 20 mol % Mo can be described by the simplified scheme

 $8NaPO_3 + 2Mo \longrightarrow MoP$ 

$$+ 0.5 Mo_2 O_5 \cdot 4 Na_2 O \cdot 3.5 P_2 O_5$$

where the resulting phosphates are represented as mixed oxides.

The other alkali-metal polyphosphates react with Mo in a similar way. The reduction of sodium cyclotriphosphate by tungsten, the closest analog of Mo, yields WP.

## CONCLUSION

The reaction between sodium cyclotriphosphate and Mo metal at temperatures above 650–700°C yields MoP and depolymerized phosphates.

The lowest content of unreacted Mo in the reaction products is observed when mixtures containing less than 20 mol % Mo are reacted at 1000°C for 0.5 h.

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