

## LETTERS TO THE EDITOR

### Low-Temperature Hydrothermal Reduction of Ammonium Paratungstate

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Ammonium paratungstate has been found to reduce to an ammonium tungsten bronze when hydrothermally treated at 200°C in nonaqueous solvents, such as acetic acid. It has the hexagonal bronze structure with lattice parameters similar to the high-temperature preparations. © 1991 Academic Press, Inc.

#### Introduction

Hydrothermal synthesis has become a popular and important technique (1, 2) in solid state chemistry. It allows (3, 4) for the formation of novel compounds that cannot be formed by traditional high-temperature solid state reactions. During the course of studying (3) the hydrothermal synthesis of various tungstates, we found that ammonium paratungstate reduces to ammonium tungsten bronze,  $(\text{NH}_4)_x\text{WO}_3$ , at 200°C in nonaqueous solvents.

The tungsten trioxides and their alkali-metal-intercalation products  $M_x\text{WO}_{3+x}$  have attracted considerable attention over the years because of the variety of crystalline structures they can take up and because of their electrochemical and electronic properties, which make them attractive as active electrodes in electrochromic displays and as electrocatalysts.

#### Experimental

The reaction was carried out in a 45-ml Parr acid digestion bomb filled to 70% of capacity with solvent and 3 g of ammonium paratungstate,  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$ , obtained from Alfa Chemical. The solvents used were glacial acetic acid, ethylene glycol, and a 2:1 ethylene glycol/acetic acid mixture. The reaction took place at 200°C for 5 days at autogenous pressure. Shorter reaction times did not lead to complete reduction of the product, and longer times did not improve the reduction. The dark blue product was filtered and washed with acetone, then stored in a glovebox under nitrogen. The compound rapidly oxidizes in air. The pressure of the acetic acid reaction is approximately 8 atm, whereas for ethylene glycol the pressure is slightly above 1 atm.

X-ray powder diffraction was performed on a Rigaku/Siemens diffractometer at 1° of 2θ/min, and lattice parameters were determined by least-squares analysis. The ammo-

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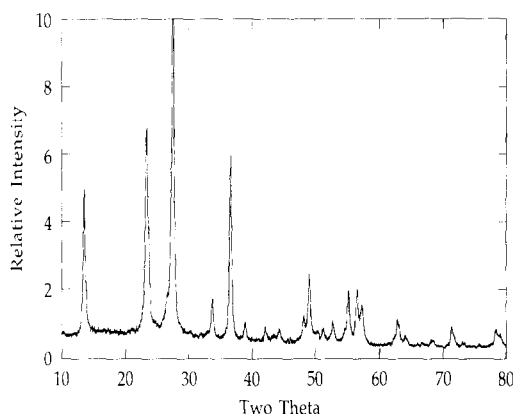


FIG. 1. X-ray powder diffraction pattern of the ammonium tungsten bronze (CuK $\alpha$  radiation).

nia content was determined by Keldjal's method. The amount of reduced tungsten(V) was determined by the method of Choain and Marion (5), in which Ag<sup>+</sup> is reduced to silver metal by the reduced tungsten which is oxidized to W(VI). The silver metal is reacted with nitric acid and titrated with potassium thiocyanate.

## Discussion

X-ray powder diffraction (Fig. 1) showed that the product of the glacial acetic acid and the 2:1 mixture reactions were single phase, and were indicative of a hexagonal tungsten bronze structure. The reaction with ethylene glycol produced two phases which were identified as the hexagonal phase and a pyrochlore phase. We are presently trying to isolate the pyrochlore fraction as a pure phase.

Ammonium tungsten bronzes are normally prepared by the reduction of ammonium paratungstate in hydrogen (6). In this gas/solid reaction reduction does not commence until 290°C and the reaction is not complete until 400°C, almost double the temperature reported here. Ammonium

tungsten bronze has also been prepared (7) hydrothermally by the reaction of tungsten metal, tungsten trioxide, and ammonium hydroxide at 700°C and 3 kbar pressure, of considerably higher temperatures and pressures than reported here. The X-ray lattice parameters (Table I) of the ammonium tungsten bronzes formed here are similar to those reported earlier (6, 7).

Infrared spectroscopy showed an absorption at 1400 cm<sup>-1</sup>, which is indicative of an ammonium ion. The ammonium content determined by the Kjeldahl method was found to be 0.30 NH<sub>4</sub><sup>+</sup>/W. The degree of reduction depended upon the solvent mixture used. For the reactions in acetic acid and in 2:1 ethylene glycol/acetic acid the reduced tungsten(V) was determined to correspond to the formulas (NH<sub>4</sub>)<sub>0.30</sub>WO<sub>3.03</sub> and (NH<sub>4</sub>)<sub>0.30</sub>WO<sub>3.06</sub>, respectively. The reduced tungsten content was not determined for the ethylene glycol mixture due to the presence of two phases, but the color was brown, compared to dark blue for the other two, which indicates a lower degree of reduction.

For the reduction to take place it appears that the ammonium in the paratungstate reacts with the organic medium, probably forming an amide or an amine, and releasing active hydrogen, which is the reducing agent. All the solvents were clear before the reduction and were a murky dark brown after reaction, indicative of solvent reaction

TABLE I  
X-RAY PARAMETERS OF HEXAGONAL PHASE

| Organic medium    | Lattice parameters    |                       |
|-------------------|-----------------------|-----------------------|
|                   | <i>a</i> <sub>0</sub> | <i>c</i> <sub>0</sub> |
| Acetic acid       | 7.402(4)              | 7.541(6)              |
| Ethylene glycol   | 7.45                  | 7.55                  |
| 2:1 mixture       | 7.354(6)              | 7.551(7)              |
| Hydrogen (6)      | 7.388(3)              | 7.551(6)              |
| High pressure (7) | 7.395                 | 7.525                 |

with the ammonium paratungstate, or self-polymerization. Infrared, and  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy were used to determine the source of the reduction. The NMRs were complicated and, except for the reaction using only acetic acid, indicated that all of the starting organic reactants were consumed.

Pressure affects the degree of reduction and as stated earlier glacial acetic acid heated at  $200^\circ\text{C}$  produces a vapor pressure of about 8 atm, whereas ethylene glycol produces no vapor pressure. The reaction in acetic acid reduced the tungsten to the greatest degree, followed by the ethylene glycol/acetic acid mixture, whereas ethylene glycol alone produced very little reduction of the tungsten. An oxidized ammonium pyrochlore  $[(\text{NH}_4)_2\text{O}]_x\text{W}_2\text{O}_6$  has been prepared (8) from ammonium paratungstate in an ethylene glycol solvent acidified with acetic acid under ambient pressure conditions but no reduction was reported.

There appears to be a structural relationship between ammonium paratungstate, whose structure is unknown, cubic pyrochlore, and the hexagonal tungsten bronze structure. Ammonium paratungstate may not enter solution while reacting but is probably slowly reduced topotactically while it remains at the bottom of the reaction vessel. In the one case where two phases were observed, it is possible that ammonium paratungstate either transformed into the pyrochlore phase before the hexagonal phase or

vice versa. We are now studying this relationship to see if this is indeed the case and possibly, to obtain some ideas about the paratungstate structure.

We have shown that ammonium paratungstate can be reduced in nonaqueous solvents to ammonium tungsten bronze. This is the first report of a hydrothermal reduction of tungsten oxides at such low temperatures and pressures; we expect that this should be a generally applicable reaction that might lead to some new structures.

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#### References

1. Y. YONG AND P. WENQIN, *J. Chem. Soc. Chem. Commun.* 1166 (1990).
2. Y. YONG AND P. WENQIN, *J. Chem. Soc. Chem. Commun.* 764 (1990).
3. K. P. REIS, A. RAMANAN, AND M. S. WHITTINGHAM, *Chem. Mater.* **2**, 219 (1990).
4. R. C. HAUSHALTER AND F. W. LAI, *Angew. Chem. Int. Ed. Engl.* **28**, 743 (1989).
5. C. CHOAIN AND F. MARION, *Bull. Soc. Chim. Fr.* 212 (1963).
6. P. G. DICKENS, A. C. HALLIWELL, D. J. MURPHY, AND M. S. WHITTINGHAM, *Trans. Faraday Soc.* **67**, 794 (1971).
7. T. E. GIER, D. C. PEASE, A. W. SLEIGHT, AND T. A. BITHER, *Inorg. Chem.* **7**, 1646 (1968).
8. A. COUCOU AND M. FIGLARZ, *Solid State Ionics*, **28-30**, 1762 (1988).