# Decomposition of Blue Orthorhombic Hydrogen Molybdenum Bronze, $H_{0.30}MoO_3$, by Heating *in vacuo* and in Helium Gas

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The decomposition process of orthorhombic hydrogen molybdenum bronze, $H_{0.30}MoO_3$, was studied by the temperature programmed decomposition (TPD) technique *in vacuo* and in helium gas. The only gas liberated during the decomposition was $H_2O$ and no other gas was detected. The TPD spectrum above 150 °C was composed of three bands (PII, PIII, and PIV). The PII band corresponded to the process from $H_{0.30}MoO_3$ to $H_{0.21}MoO_{2.95}$ without any structural change. The PIII band corresponded to the process from $H_{0.21}MoO_{2.95}$ to $H_{0.06}MoO_{2.88}$ with the structural change and the PIV band, to the process from $H_{0.06}MoO_{2.88}$ to $MoO_{2.85}$.

It is well known that hydrogen molybdenum bronzes are formed by reduction of $MoO_3$ in an aqueous medium[1] or by atomic hydrogen.[2] There are many phases which may be formulated as $H_xMoO_3(0<x\leqq2.0)$. The existence of four phases has been confirmed by Birtill and Dickens.[3] According to them, the ranges of homogeneity of these phases with the approximate limits are as follows; (i) blue orthorhombic ($0.23<x<0.40$), (ii) blue monoclinic ($0.85<x<1.04$), (iii) red monoclinic ($1.55<x<1.72$), and (iv) green monoclinic ($x=2.0$). In the hydrogen molybdenum bronze, hydrogen is inserted into the $MoO_3$ layers as atoms[4—6] and occupies available sites near the zigzag oxygen atoms of the intralayers.[6]

The authors have studied the structural and compositional changes of the blue orthorhombic bronze heated *in vacuo* and found that the bronze is decomposed to a nonstoichiometric compound with a rhombic $MoO_3$ structure with the evolution of $H_2O$.[7]

Sermon *et al.*[8] and Marcq *et al.*[9] studied the catalytic hydrogenation reaction for 1-pentene and ethylene on the red monoclinic bronze, $H_{1.6}MoO_3$, obtained from Pt-supported $MoO_3$ by hydrogen spillover. They concluded that atomic hydrogen plays an important role in the catalytic hydrogenation. The hydrogen in the blue orthorhombic bronze is also effective for 1-butene isomerization.[10]

It is important in studying the catalytic reaction to reveal the decomposition process of the bronze and the behavior of hydrogen in the bronze on heating. The authors have reported[11] the kinetics of isothermal decomposition of the blue orthorhombic bronze. In the present work, the decomposition was studied by the temperature programmed decomposition (TPD) technique *in vacuo* and in helium gas.

## Experimental

The sample was prepared by the Glemser's method.[1] Its structure was confirmed by X-ray diffraction analysis to be identical with the blue orthorhombic phase reported by Birtill and Dickens.[3] The composition was determined to be $H_{0.30}MoO_3$ by chemical analysis[12] and by thermogravimetry.

A conventional high vacuum system equipped with a Cahn microbalance, a Pirani gauge, and a quadrupole gas analyzer was used for the measurements of the changes in weight and pressure. The rate of heating, $\beta$, was controlled by a temperature programmed controller.

The decomposition of the blue orthorhombic bronze on heating in helium gas was also studied by a gas chromatograph.

A differential scanning calolimeter (DSC) was used for measuring the heat of decomposition in helium gas.

## Results

*Temperature Programmed Decomposition* in vacuo *(TPD(v)).* The bronze, $H_{0.30}MoO_3$, was degassed at room temperature under a vacuum of $10^{-4}$ Torr for 2 h and then heated at various heating rates ($\beta$=3.5—13.7 °C min$^{-1}$). The change in pressure was recorded with a Pirani gauge. The TPD(v) spectra at the various heating rates are shown in Fig. 1. A small band appeared below 150 °C. The TPD (v) spectrum above 150 °C showed clearly three peaks as the rate of heating was slow. Indeed, the spectrum obtained at a heating rate of 3.5 °C min$^{-1}$ showed three distinct peaks, suggesting that the spectrum may be composed of three bands and the line shapes of each band may

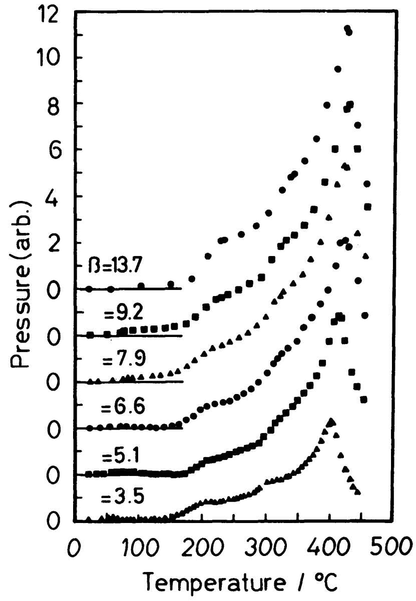


Fig. 1. TPD(v) spectra of the blue orthorhombic bronze, $H_{0.30}MoO_3$.

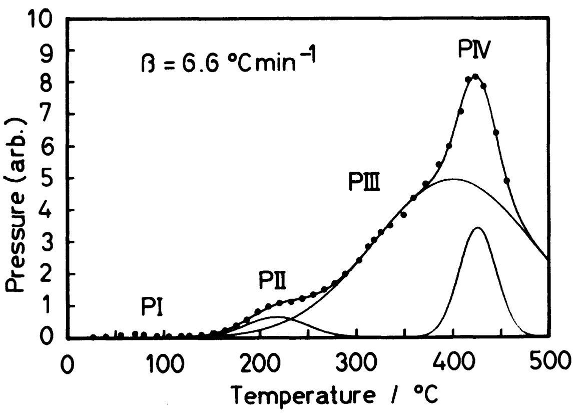


Fig. 2. Analysis of TPD(v) spectrum of the blue orthorhombic bronze, $H_{0.30}MoO_3$.

be symmetrical. Therefore, the spectra above 150 °C could be analyzed by a curve resolver. One of the results is shown in Fig. 2. This shows that the spectrum above 150 °C consists of three bands (PII, PIII, and PIV). All the spectra in Fig. 1 were analyzed by the same technique. The shifts of each peak temperature (Tm) to higher temperatures were observed when the heating rates were increased. The peak temperatures, Tm(II) of the PII band appeared over a temperature range of 185—238 °C. Tm(III) of the PIII band and Tm(IV) of the PIV band appeared at 356—408 and 392—429 °C, respectively.

The gas liberated in these experiments was $H_2O$ and no other gas was detected by the quadrupole gas analyzer. The above results suggest that hydrogen in the bronze reacted with the lattice oxygen to produce $H_2O$ in three steps.

Activation energies of 18.4(PII), 28.4(PIII), and 39.6(PIV) kcal mol$^{-1}$ were estimated from the shifts of the peak temperatures (Tm(II), Tm(III), and Tm (IV)).[13]

*Thermogravimetry.* The weight-loss of the blue orthorhombic bronze was measured by a Cahn microbalance at various heating rates ($\beta$=3.5—13.7 °C min$^{-1}$) *in vacuo*. The X-ray and thermogravimetric results showed that on the vacuum heating the bronze transformed to $MoO_{2.85}$, a nonstoichiometric compound with rhombic $MoO_3$ structure, through a mixture of the orthorhombic and rhombic structures[7] as follows;

$$\text{(I)}\quad H_{0.30}MoO_3\cdot nH_2O \xrightarrow{\text{below } 150\,^{\circ}\mathrm{C}} H_{0.30}MoO_3$$

$$\text{(II)}\quad \xrightarrow{\approx 286\,^{\circ}\mathrm{C}} H_{0.21}MoO_{2.95}{}^{**}$$

$$\text{(III)}\quad \xrightarrow{\approx 390\,^{\circ}\mathrm{C}} H_{0.06}MoO_{2.88}{}^{***}$$

$$\text{(IV)}\quad \xrightarrow{\approx 446\,^{\circ}\mathrm{C}} MoO_{2.85}\,.$$

**: Orthorhombic bronze with the lowest hydrogen content.

***: Isomorphous with rhombic $MoO_3$.

The rising temperature technique has been widely used in kinetic investigation of thermal decomposition and other reactions of solid.[13—16] By this technique, Ozawa[16] formulated a simple and useful method to analyze the thermogravimetric data and determined the activation energies of the decomposition of calcium oxalate and the degradation of Nylon 6. According to his method, activation energies are easily determined as follows; initially the fraction reacted, $\alpha$, is plotted against the reciprocal absolute temperature ($1/T$), and the value of $1/T$ corresponding to $1-\alpha$ of each heating rate curve can be estimated. Secondly, the activation energies can be determined from the plots of the logarithms of the heating rate, log $\beta$, *vs.* $1/T$ obtained from the above plots.

Figure 3 shows the typical thermogravimetric curves of the bronze plotted against $1/T$. If the decomposition proceeds in one step, activation energies estimated from the plots of log $\beta$ *vs.* $1/T$ should be equal at every $\alpha$. However, the results suggest that the activation energies for different $\alpha$ differ from one another. The value of $1-\alpha$ at the peak temperatures (Tm(II), Tm(III), and Tm(IV)) of each band of the TPD(v) spectra were 0.86±0.05(PII), 0.31±0.08(PIII), and 0.12±0.03(PIV), respectively. Figure 4 shows the plots of log $\beta$ *vs.* $1/T$ which gives the same value of $1-\alpha$, corresponding to Tm(II), Tm(III), and Tm(IV). From these

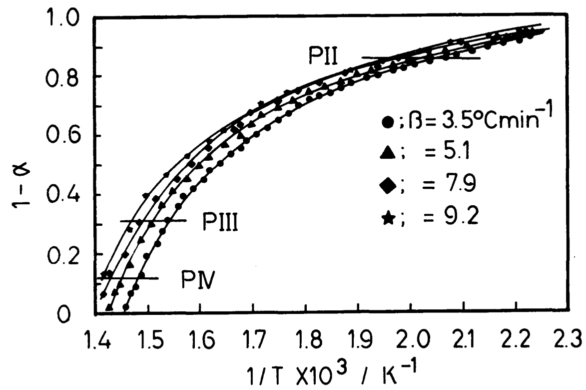


Fig. 3. The thermogravimetric curves of $H_{0.30}MoO_3$ plotted against the reciprocal absolute temperatures.

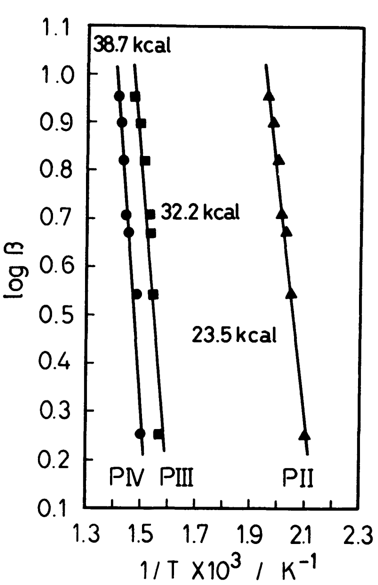


Fig. 4. The plots of logarithms of heating rates against the reciprocal absolute temperatures.

plots, the activation energies were determined to be 23.5(PII), 32.2(PIII), and 38.7(PIV) kcal mol$^{-1}$, respectively. These values are in good agreement with those determined from the TPD(v) spectra.

*Temperature Programmed Decomposition in Helium Gas (TPD(h)).* The bronze was also heated in helium gas with the flow rate of 90 ml min$^{-1}$ and was studied by means of the gas chromatograph. The heating rates employed were 3, 7.5, and 10 °C min$^{-1}$. No peak appeared below 200 °C. Above this temperature, however, three peaks appeared as in the case of vacuum heating. The range of Tm(II) was 259—283 °C, which was higher compared with that obtained by TPD(v) spectra. Those of Tm(III) and Tm(IV) were 296—315 and 352—380 °C. These were lower than those obtained by TPD(v) spectra. These differences in Tm may be attributed to the difference in the experimental methods.

The activation energies were also estimated from the shifts of Tm and the heating rates and were determined to be 27.5(PII), 32.2(PIII), and 38.0(PIV) kcal mol$^{-1}$, respectively. The activation energy of PII is a little higher than those determined by TPD(v) spectra and by thermogravimetry, but those of PIII and PIV are in good agreement.

*DSC Measurement.* The heat of decomposition of the bronze was measured by DSC with the heating rates of 5, 7, and 10 °C min$^{-1}$, which were treated in helium gas with the flow rate of 90 ml min$^{-1}$. Three endothermal peaks appeared at 240—250, 310—321, and 353—364 °C, and were in good agreement with those of the Tm(II), Tm(III), and Tm(IV) of TPD(h) spectra obtained by heating in helium gas. The total endothermal heat was determined by the peak area to be 5.82±0.13 cal g$^{-1}$. If this value were proportioned to each band area of PII, PIII, and PIV, the alloted values would be 0.81±0.02(PII), 1.98±0.04(PIII), and 3.03±0.07(PIV) cal g$^{-1}$, respectively. These energies produce many effects; heat of reaction between hydrogens and lattice oxygens, heat of desorption of $H_2O$, *etc.* Therefore, it is difficult to conclude that the endothermal heats are directly related to the binding energies of hydrogen in the bronze.

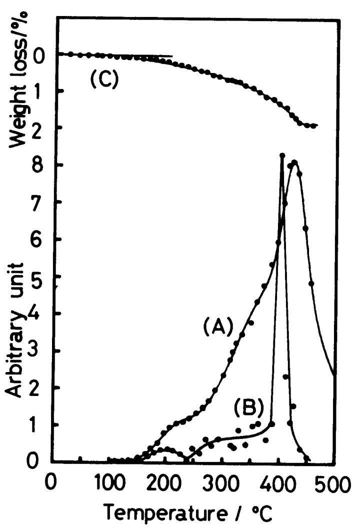
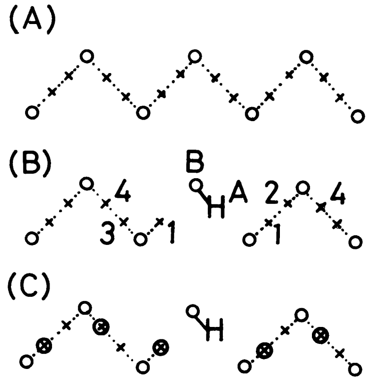


Fig. 5. Comparison between the TPD(v) spectrum and the differential curve obtained from the change in weight. (A); TPD(v) spectrum, (B); differential curve, and (C); change in weight.



O: Oxygen atom, ×: available hydrogen site, ⊗: most available hydrogen site.

Fig. 6. Model of the available hydrogen atom sites in the blue orthorhombic bronze. (A); The average structure, (B); four kinds of available hydrogen atom sites apart from the A site occupied by a hydrogen atom near the oxygen(B), and (C); most available hydrogen atom sites.

## Discussion

Figure 5(A) shows the typical TPD(v) spectrum obtained by the Pirani gauge, while Fig. 5(B) is the differential curve calculated from the weight change (Fig. 5(C)) of the bronze on vacuum heating. As shown in Fig. 5(B), the fluctuation is recognized above 250 °C and it is difficult to obtain a smooth curve. On the other hand, the TPD(v) spectrum is very smooth. However, the Tm's are somewhat higher than those obtained from the differentiation of the weight changes. The pirani gauge method to detect pressure change is somewhat different from the microbalance for measuring weight changes and, therefore, there might be a temperature lag between the both measurements. However, the Tm's obtained from both measurements might occur with a similar temperature lag in all the steps. The TPD method gives the smooth spectrum, and is the simplest and most useful method for studying the decomposition of the bronze.

According to the proton NMR result,[11] there is no difference in the behavior of the protons in the original bronze and in the bronze treated at 350 °C under a vacuum of $10^{-4}$ Torr (1 Torr=133.322 Pa). This suggests that the environment surrounding the protons does not change during heating at 350 °C. The hydrogen atom sites in the bronze are surrounded by oxygen atoms making zigzag chains in the $MoO_3$ layers, as is illustrated in Fig. 6(A). Two hydrogen atom sites on a given O···O line are too close for two hydrogen atoms to occupy them simultaneously and inelastic neutron scattering has confirmed that there is no $OH_2$ groups in this phase.[17] If one hydrogen atom occupied the A site near oxygen (B) as shown in Fig. 6(B), there would be four available sites for the hydroxyl hydrogen.[6] Most of the hydrogen atom must have a neighbouring site 1 in pairs.[6] Therefore, the most available site must be the site 1 or 4 as shown in Fig. 6(C).

The PI band which appears below 150 °C in the TPD(v) spectra may result from the desorption of a small amount of adsorbed water. This corresponds exactly to the I process.

The orthorhombic bronze retains its original crystal structure up to about 287 °C although the hydrogen content ($x$) changes from 0.30 to 0.21. This suggests that the reaction occurs sporadically and the nearest two hydrogen atoms in the sites 1 and 4 react with the nearest lattice oxygens to produce $H_2O$. This temperature range falls in that of the PII band in the TPD spectra and, therefore, the PII band corresponds to the PII process.

The weight-loss in the temperature range of about 287 and 390 °C was about a half of the total weight-loss, and the product was confirmed to be the mixture of the orthorhombic and rhombic $MoO_3$ structures. It might be considered that the dehydration of the PII process involves nucleation and the nuclei produced might accelerate the dehydration successively. On the other hand, the PIII band is broad and the integrated area is much larger than those of the PII and PIV. Considering the above results, it is concluded that the PIII band corresponds to the PIII process.

$H_{0.06}MoO_{2.88}$ was isomorphous with the rhombic $MoO_3$ and the hydrogen atoms were considered to be sparsely distributed. Therefore, even though $H_{0.06}MoO_{2.88}$ was decomposed completely to $MoO_{2.85}$ at about 446 °C with the evolution of $H_2O$, no structural change was observed. The decrease in weight was small and the PIV band was narrow and small. It is reasonable to conclude that the PIV band corresponds to the IV process.

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