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Thermic investigations of hexagonal hydrogen bronze, H_xWO_3

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The thermic–kinetic behaviour of hydrogen tungsten bronze, H_xWO_3, was investigated by differential scanning calorimetry and X-ray analysis. It is shown that the thermal decomposition of bronze into hydrogen and WO_3, is exothermic. Further, it is shown that the hexagonal WO_3 system is exothermally transformed (irreversibly) to the monoclinic WO_3 system. Activation energies, frequency factors and rate constants of the corresponding processes are determined. It is shown that the hexagonal WO_3 system adsorbs hydrogen at approximately 480 K, and desorbs at room temperature in air or an argon–nitrogen atmosphere. It is also shown that H_xWO_3 is unstable and that it decomposes with time, forming brown WO_3 which gives no yellow modification during the WO_3 phase transformation. The newly formed modification adsorbs hydrogen without changing colour.

1. Introduction

Oxide bronzes, A_xMO_n, belong to the class of ternary oxide phases (materials) formed by building an electropositive element A into the oxide matrix MO_n of a transition metal M [1]. Examples of oxides that form oxide bronzes which are of special interest are WO_3, MoO_3 and V_2O_5. The metal denoted A is most frequently an alkali metal, but instead of an alkali metal hydrogen may be introduced and then a hydrogen bronze, H_wWO_3, is formed [2, 3]. If there is no change in the oxidation state of the components when Metal A is introduced into the matrix MO_n, and Metal A is present inside the oxide matrix only in the "dissolved" and inert form as in Na_xWO_3 ($x > 0.3$), then such a bronze has electrical conductivity of the metallic type. Owing to their electrical and certain other properties, oxide bronzes represent a new and important electrode material in electrochemistry. Bronze syntheses are most frequently performed by standard methods during solid-state reactions in appropriate atmospheres, and also by molten salt electrolysis. Hydrogen tungsten bronze is obtained by the zinc reduction of WO_3 in HCl and molybdenum by the reaction between Mo, MoO_3 and H_2O inside a sealed tube [4]. However, the possibility of obtaining hydrogen bronze by solid-state reaction according to the relation $CuO + WO_3 = CuWO_4$ and afterwards by hydrogen reduction to copper and hexagonal H_xWO_3 phase should pointed out; copper is separated by dissolving in HNO_3, and during this separation a brown–blue sediment, hexagonal H_xWO_3, remains as the precipitate [5]. Products obtained from this kind of process are identified by X-ray diffraction analysis (Fig. 1).

The same bronze as this one can be obtained from hexagonal WO_3, formed by thermic decomposition of $WO_3 \cdot \frac{1}{3}H_2O$, and hydrogen reaction in the presence of platinum [6, 7], or on the basis of hydrogen spillover from platinum to trioxide supports (WO_3 and MoO_3); in this way hydrogen bronzes of types H_xWO_3 and H_xMoO_3 with maximal values of $x = 0.46$ and 1.63, respectively, are obtained [8–10].

Calorimetric investigations of the bronze-forming reaction, using also thermal cycles [1], give us the following thermodynamic enthalpy and Gibbs free energy values:

$$\tfrac{1}{2}H_2(g) + (1/x)WO_3(s) = (1/x)H_xWO_3(s)$$

with $x = 0.35$, $\Delta H^0 = -9.6\,\mathrm{kJ\,mol^{-1}}$; $(1/x)\Delta H^0 = -27.4\,\mathrm{kJ\,mol^{-1}}$, $(1/x)\Delta G^0 = -9.1\,\mathrm{kJ\,mol^{-1}}$; and

$$\tfrac{1}{2}H_2(g) + (1/x)MoO_3(s) = (1/x)H_xMoO_3(s)$$

with $x = 0.3$, $\Delta H^0 = -12.1\,\mathrm{kJ\,mol^{-1}}$; $(1/x)\Delta H^0 = -40.3\,\mathrm{kJ\,mol^{-1}}$, $(1/x)\Delta G^0 = -20.8\,\mathrm{kJ\,mol^{-1}}$.

Our research was directed towards the thermic–kinetic behaviour of bronze obtained according to the method of Solonin and Privalor [5].

2. Experimental procedure

Hydrogen bronze, H_xWO_3, synthesized according to the method of Solonin and Privalor [5], was used in powder form. Thermic investigations were done with a DuPont Thermal Analyser 1090 using the scanning calorimetric method, while X-ray analysis was done with a Philips PW 1051 diffractometer using Cu$K\alpha$ radiation and a graphite monochromator. The kinetics of the thermal process were investigated according to the method of Broker [11], based on the change of the temperature maximum on the thermogram with change in the heating rate β. According to

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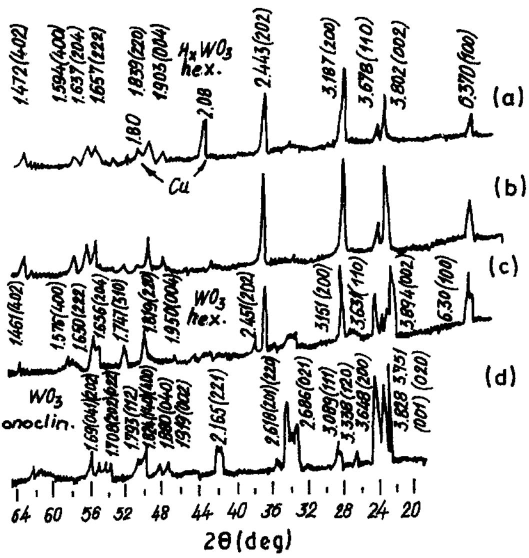

Figure 1 X-ray diffractograms of products obtained during hydrogen bronze synthesis [5]: (a) after hydrogen reduction, (b) after copper dissolution, (c) after heating in air to 400° C (673 K), (d) after heating above 500° C (773 K). Spacings in Å (1 Å = 0.1 nm).

this method, log (β/T^2) against $1/T$ is a straight line with a slope $\Delta \log (\beta/T^2)/\Delta(1/T) = -E/R$, where E is the activation energy and T the temperature at the maximum. From these data the frequency factor, $Z = [\beta E \exp (E/RT)]/RT^2$, and the rate constant of the process, $k = z \exp(-E/RT)$, can be determined. The second method used was the non-isothermal analysis of the thermogram [12] recorded during differential thermic analysis (DTA), differential enthalpy (DEA) or differential scanning calorimetry (DSC) applied for chemical reaction analysis. On the basis of these theoretical considerations, for the rate constant of the first-order reaction the following equations are valid:

$$\begin{aligned} k &= \Delta T/(A - a) \\ k &= (\mathrm{d}H/\mathrm{d}T)/(A - a) \quad \text{or} \qquad (1) \\ k &= \Delta(\mathrm{mW})/(A - a) \end{aligned}$$

where H is the enthalpy, A the total area under the maximum on the thermogram, a the part of this area limited by the time t of the process duration until a temperature T was reached; ΔT, $\mathrm{d}H/\mathrm{d}t$ and $\Delta(\mathrm{mW})$ are the ordinates of the thermogram: temperature change and enthalpy change, i.e. the change in the heat of reaction for time t in units of J sec^{-1} or milliwatts. For Δ first-order reaction Equation 1 gives a straight line. From the slope $\Delta(\log k)/\Delta(1/T) = -E$ the activation energy can be obtained, while the frequency factor Z can be obtained from the relation $k = Z \exp(-E/RT)$.

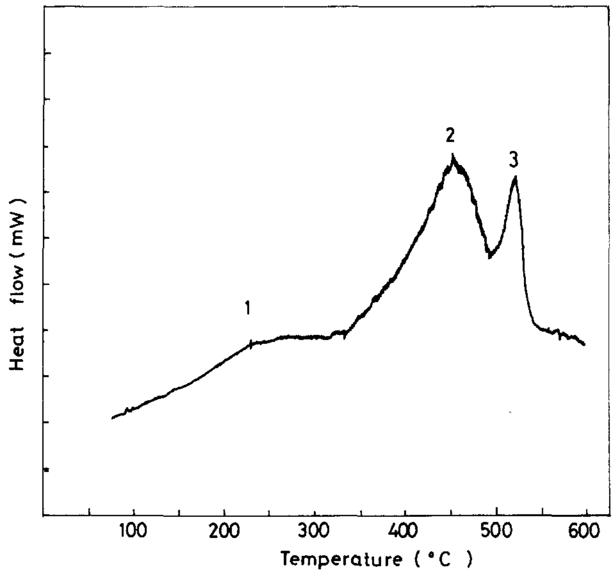

Figure 2 DSC thermogram of H_xWO_3 in argon, 15 k/min^{-1} (June 26th 1985).

3. Results and discussion

A characteristic DSC thermogram of the hydrogen bronze H_xWO_3 in an argon atmosphere is shown in Fig. 2. Three exothermal maxima, marked 1 to 3, corresponding to the process of thermic bronze transformation to yellow monoclinic WO_3, can be seen. At present we do not know to which process the first broad maximum that appears, in all used samples, during the first heating in nitrogen or argon corresponds; the second maximum corresponds to the decomposition of hexagonal hydrogen bronze with simultaneous hydrogen evolution and formation of metastable hexagonal WO_3 [5] which is faintly coloured yellow, while the third maximum corresponds to the transformation of the hexagonal WO_3 to monoclinic stable WO_3, coloured yellow.

From the straight-line dependence log (β/T^2) against $1/T$, (Fig. 3) and the slope $\Delta[\log (\beta/T^2)]/\Delta(1/T)$, the activation energies and frequency factors of single processes were found and are given in Table I.

The enthalpy for the first process is visibly dependent on the heating rate. Showing no significant effect on enthalpy, at six different heating rates, for the second and the third stage these values are given as an average of six measurements. Rate-constant values calculated for single-stage processes in the dependence of temperature are shown on Fig. 4. It can be inferred

TABLE I Thermic and kinetic parameters for hydrogen tungsten bronz thermic transformation

Parameter	Stage		
	1	2	3
Slope	-6.21×10^3	-7.38×10^3	-11.92×10^3
E(kJ mol^{-1})	118.689	141.210	227.879
Z(min^{-1})	3.024×10^{12}	7.760×10^9	5.930×10^{14}
$-\Delta H$(J g^{-1})	1.09(30), 1.31(25) 2.18(20), 4.70(15)	50.63	

*Heating rates (K min^{-1}) given in brackets.

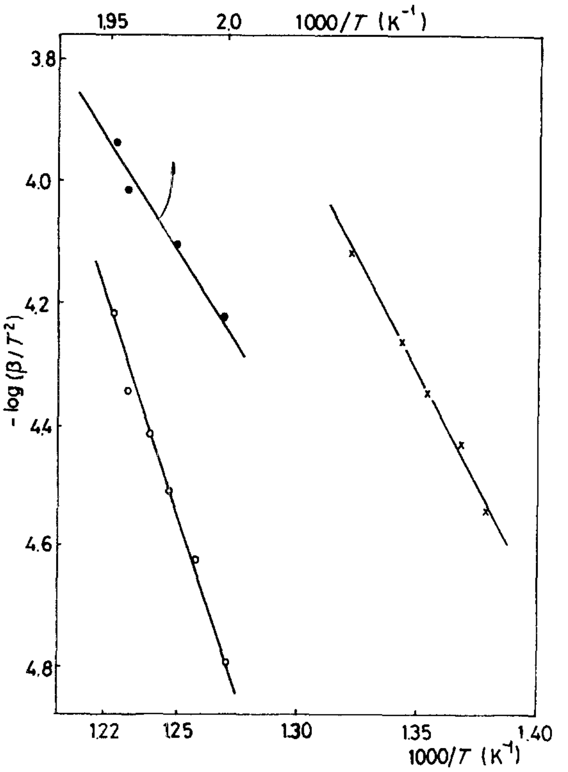

Figure 3 Plot of log (β/T^2) against $1/T$ for the different processes in Fig. 2: (●) Stage 1, (x) Stage 2, (○) Stage 3.

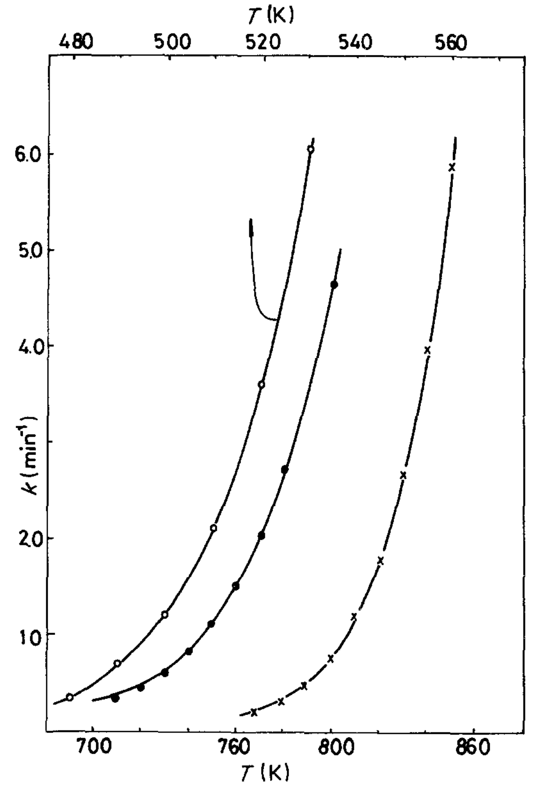

Figure 4 Temperature dependence of rate constants: (○) Stage 1, (●) Stage 2, (x) Stage 3.

that for all three stages the rates are rather high and that in the temperature maximum range these rates are only slightly different: $k_1 = 1.2$ (500 K), $k_2 = 0.44$ (720 K) and $k_3 = 0.51$ (790 K) min^{-1}. Fig. 5 shows a kinetic analysis of the exothermic Maximum 2 from Fig. 2, along with the approximate graphical separation from Maximum 3, according to Equation 1. From the slope $\Delta \log k/\Delta(1/T)$ of the thermograms obtained at different heating rates ($\beta = 10$ to $40\,\mathrm{K\,min^{-1}}$) an average activation energy of 132.4 kJ mol^{-1} is found. However, it should be pointed out that for this maximum a somewhat less expressed process precedes it which is observed at the beginning of Maximum 2 (Fig. 2). From Fig. 5 it can be seen that at lower temperatures, corresponding to the beginning of Maximum 2, the straight-line slopes are changed and for activation energy a value of $E = 88.10\,\mathrm{kJ\,mol^{-1}}$ is obtained. If this beginning of Maximum 2 is graphically corrected and straightened, then a straight line with one slope is obtained as shown in Fig. 5 (square symbols).

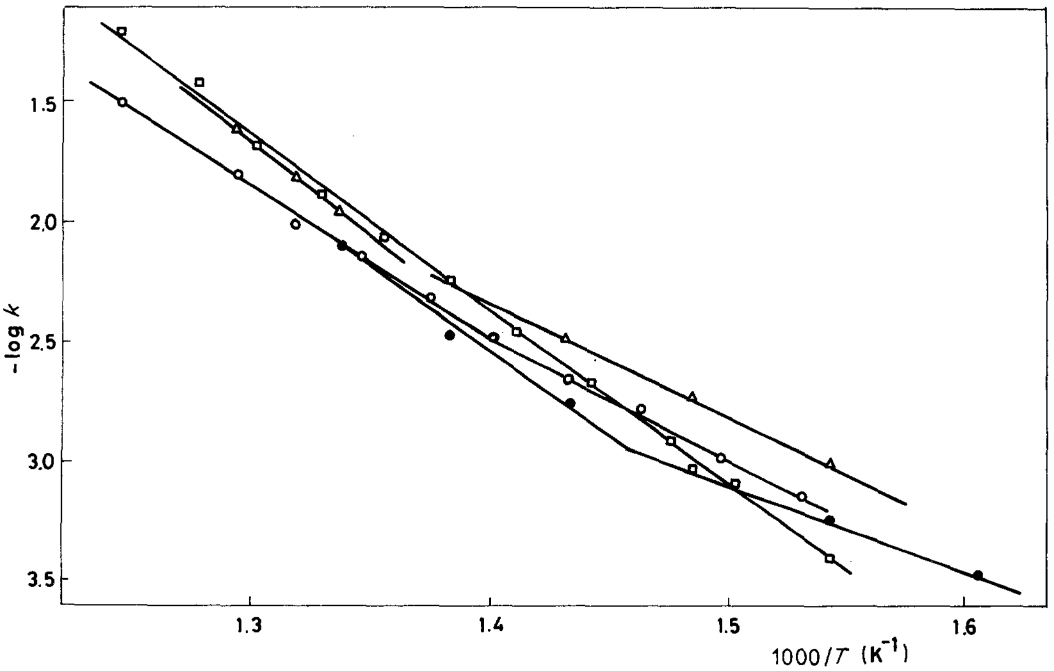

Figure 5 Kinetic–thermodynamic analyses of Stage 2 (from Fig. 2) according to Equation 1 for different heating rates (K/min^{-1}): (●) $\beta = 10$; (○) $\beta = 25$; (△) $\beta = 40$; (□) $\beta = 40$, maximum beginning and end-corrected (see text).

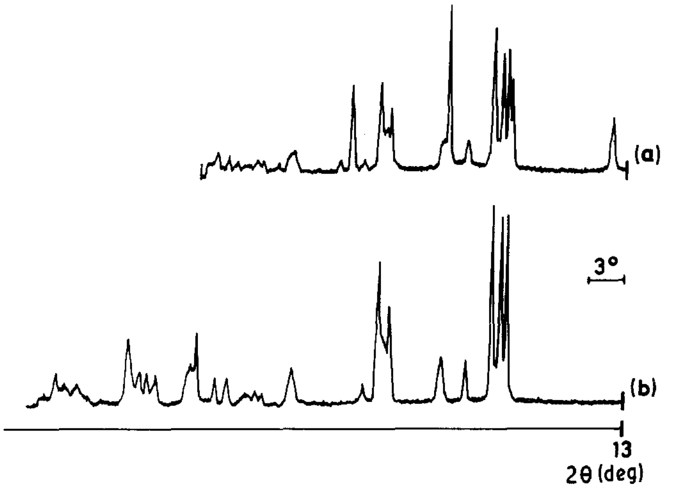

Figure 6 X-ray diffractograms: H_xWO_3 bronze heated to (a) 400° C (673 K), (b) 550° C (823 K) (without delay at final temperature).

Fig. 6 shows X-ray analyses of samples heated inside the DSC cell to pre-determined temperatures corresponding to single stages of the process. There is a distinct difference between the diffractograms of Figs 6a and b; Fig. 6a corresponds to the hexagonal WO_3 phase, while Fig. 6b corresponds to the monoclinic WO_3 phase (coloured yellow), and this is in accordance with the diffractograms of Figs 1c and d.

3.1. Sample ageing

A remarkable change in these same H_xWO_3 samples (Fig. 7b) is observed by examining them in argon after 15 months have passed. Only the third exo-maximum with the same activation energy $E = 222.60\,\mathrm{kJ\,mol^{-1}}$ (according to the method of Broker [11]) is seen. The first and the second maxima are shown but only in traces. However, during the phase transformation from hexagonal to monoclinic (Maximum 3), there is no visible change in colour, so that the product obtained has the same colour as it had before transformation. The product formed in this way adsorbs hydrogen (Fig. 8), which when kept in air or nitrogen or argon atmosphere is desorbed at room temperature.

An H_xWO_3 sample previously heated up to 400° C (673 K) in air, so as to remove hydrogen (see Fig. 2.) whose thermogram is shown in Fig. 7c, was examined again after 9 months and shows notable changes (Fig. 7d). Only the third maximum is seen with the first and second one in traces. The final heating product in nitrogen or argon has a dark colour, although the presence of the third maximum is evidence of reorganization of hexagonal to a monoclinic structure which adsorbs hydrogen (Fig. 8).

A special yellow (monoclinic) modification, a WO_3 sample heated in argon, shows neither thermic effect nor change in colour but adsorbs hydrogen after heating in nitrogen or argon like the previous samples did, and changes from a yellow colour to a brown one. It should be emphasized that all samples heated in hydrogen gain a brown colour and become hydrogen-active (Fig. 8).

Kinetic and thermodynamic magnitudes of the hydrogen adsorption process were determined by the method according to Equation 1. Fig. 9 shows the $\log k$ against $1/T$ dependence for hydrogen adsorption exo-maxima from Figs 8b and c. The activation energy for hydrogen adsorption by a sample previously heated in air to 400° C (673 K), and after 9 months of ageing heated in argon to 600° C (873 K), is $51.55\,\mathrm{kJ\,mol^{-1}}$, while the activation energy for hydrogen adsorption by yellow WO_3 previously heated in argon to 600° C (873 K) is $86.47\,\mathrm{kJ\,mol^{-1}}$. We suppose that the hydrogen adsorption process depends on the degree of sample activation which affects the changes in activation energy too. On the basis of these data it can be concluded that the H_xWO_3 sample investigated, obtained

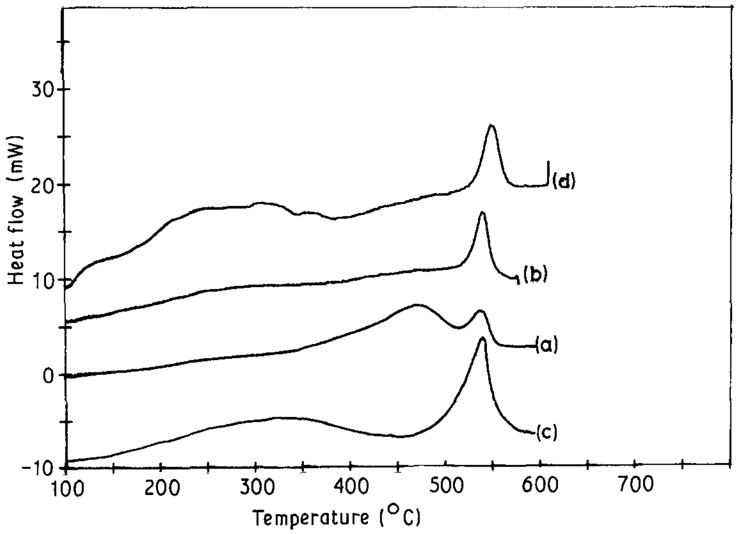

Figure 7 Sample ageing effects on DSC thermograms in argon. H_xWO_3: (a) June 26th 1985, (b) September 24th 1986. H_xWO_3 previously heated to 400° C (673 K): (c) December 6th 1985, (d) September 5th 1986.

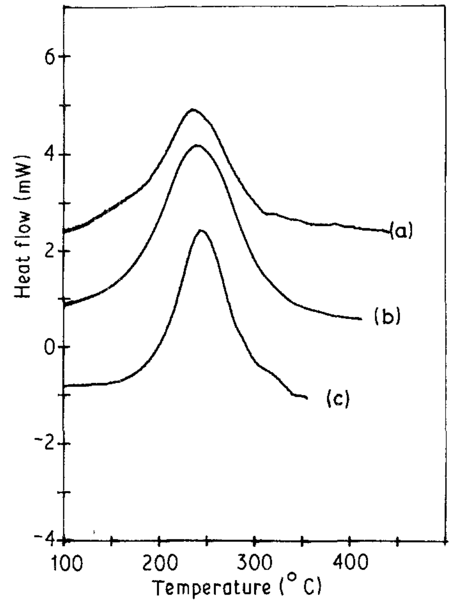

Figure 8 DSC thermograms in hydrogen: (a) sample from Fig. 7b, (b) sample from Fig. 7c and (c) yellow WO_3 sample after heating in argon to 600° C (873 K). Because of different sample weights maximum heights cannot be compared. Ordinate sensitivity: (a) and (c) $1\,mW\,cm^{-1}$, (b) $5\,mW\,cm^{-1}$.

in the manner already described [5] and kept in air, spontaneously liberates hydrogen and is subject to the structure changes manifested in processes to which Maximum 2 corresponds; this affects the process of Maximum 3 so that there is no change in colour as the result of transformation. There is no difference in behaviour between samples that have been aged for some time or before ageing have been heated to 400° C (673 K).

4. Conclusions

Fresh hydrogen tungsten bronze, H_xWO_3, synthesized according to the method of Solonin and Privalov [5] exhibits the following effects:

1. Heating in a nitrogen or argon atmosphere gives three exothermal effects that correspond to a hydrogen-liberating process and to an irreversible transformation of hexagonal WO_3 to yellow monoclinic WO_3.
2. Storage gives an ageing effect that leads to spontaneous hydrogen liberation and structure changes so that by heating gives only the third exo-maximum, a process which now leads to the forming of a brown WO_3 phase.
3. Independently of the ageing time, both hydrogen bronze and the pure yellow modification WO_3 heated in a hydrogen atmosphere adsorb hydrogen exothermally and gain a brown colour. Hydrogen is spontaneously desorbed at room temperature in air, nitrogen or argon.

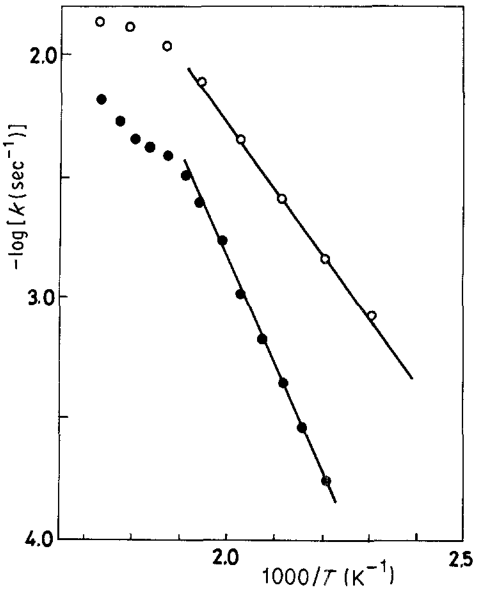

Figure 9 Plots of log k against $1/T$ for exo-maxima from (○) Fig. 8b and (●) Fig. 8c.

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