Kinetics of the Thermal Decomposition of Cobaltic Acid, CoO(OH)

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The isothermal decomposition of cobaltic acid, CoO(OH), has been examined. Two mechanisms are found to operate: above 300 °C, phase-boundary control in two dimensions dominates with an activation energy of 101 kJ mol^{-1}; below 290 °C, a nucleation and growth mechanism is appropriate, the activation energy being 214 kJ mol^{-1}. Kinetic data have been analysed by a wide variety of methods all leading to essentially the same conclusions. At all temperatures the product of decomposition is the microcrystalline spinel Co_3O_4. A preliminary study of a sample of the mineral heterogenite has also been undertaken, the activation energy obtained for its decomposition being 109 ± 20 kJ mol^{-1}. A small amount of occluded water made this work difficult.

COBALT(III) oxide hydroxide occurs in nature as the mineral heterogenite.[1] It is a rare example of a simple but stable cobalt(III) species. Its structure [2,3] consists of close-packed layers of oxide ions octahedrally surrounding cobalt(III) ions. The position of the hydrogen in this lattice is of interest as it may exemplify a short asymmetric hydrogen bond.[2]

The thermal decomposition of CoO(OH) proceeds according to equation (1). The cobalt(II)/(III) spinel produced is of interest because of its semiconductor and catalytic properties; oxygen and water separate simultaneously in this decomposition.[4]

$$12\,CoO(OH) \longrightarrow 4\,Co_3O_4 + 6\,H_2O + O_2 \qquad (1)$$

Avramov [4] studied the thermal decomposition of CoO(OH) in air in the temperature range 260—310 °C. Two phases in the decomposition were observed; one below 280 °C with an activation energy of 145 kJ mol^{-1} and one above 280 °C with an activation energy of 79 kJ mol^{-1}. The rate law for phase-boundary control in two dimensions,[5] equation (2), was used at all the

$$1 - (1 - \alpha)^{\frac{1}{2}} = kt \qquad (2)$$

temperatures studied. The change in mechanism was attributed to the electron-transfer process between oxide ion and Co^{III} becoming rate determining. We considered this to be unlikely, since a change in rate law is often associated [6] with such a marked deviation from simple Arrhenius behaviour. This possibility was not investigated by Avramov. We have thus undertaken a study of the thermal decomposition of CoO(OH) over a wider temperature range (264—391 °C). The product and starting material have been analysed by spectroscopic and diffraction methods and the choice of formal kinetic expressions carefully considered. A limited study of a sample of naturally occurring CoO(OH) [heterogenite,[1] British Museum (B.M.) Catalogue No. 1930, 980] has also been undertaken.

RESULTS

The compound CoO(OH) was prepared as described in the Experimental section and examined by *X*-ray diffraction (powder method) and i.r. spectroscopy. The results, which agree with literature data, are summarised in Tables 1 and 2. The same techniques were used to analyse the product of isothermal decomposition at a number of temperatures. The results at 264 and 341 °C are also given in Tables 1 and 2. The reaction product at all temperatures is microcrystalline Co_3O_4; observed *d* spacings and major i.r. bands again agree well with literature values.

TABLE 1

Results of *X*-ray diffraction studies: *d* spacing (Å)

CoO(OH)		Co_3O_4		
Ref. 2	This work	*	264 °C	341 °C
4.40	4.30	4.65		4.69
2.43	2.43	2.85	2.80	2.80
2.32	2.39	2.43	2.40	2.40
1.98		2.31	2.27	
1.80	1.77	1.55	1.53	1.54
1.50		1.41	1.40	1.42
1.43	1.41			
1.36	1.35			

* T. Nishina, M. Yonemura, and Y. Kotera, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3282.

Thermogravimetric analysis of oven-dried CoO(OH) at 10 °C min^{-1} under N_2 (10 cm^3 min^{-1}) revealed a mass loss of 12.8% [the theoretical value is 12.7% for $CoO(OH) \longrightarrow Co_3O_4$].

Isothermal Kinetic Studies of CoO(OH).—At temperatures >290 °C all runs were deceleratory throughout. The rate expression for phase-boundary control in two dimensions adequately describes the reaction for fractional decomposition (α), $0.05 < \alpha < 0.90$. Rate constants are summarised in Table 3 and typical plots are shown Figure 1. A wide range of methods was used to check the validity of this rate law including reduced time plots,[7] plots of $\ln - [\ln(1 - \alpha)]$ against $\ln t$ (in the region $0.1 < \alpha < 0.5$),[8] differential plots,[9] and a statistical comparison of various integrated rate equations. All methods point to the conclusion that phase boundary control in two dimensions, equation (2),

TABLE 2

Major i.r. frequencies (cm^{-1}) [a] for CoO(OH) and Co_3O_4

Co_3O_4 [b]			CoO(OH)	
[c]	341 °C	259 °C	Ref. 2	Oven dried
220				
392	392m	392m	1 800s br	1 800s br
590	570s	575s	1 221w	1 225w
672	665s	665s	578s	580w

[a] Spectra were recorded between 220 and 700 cm^{-1} for Co_3O_4 and between 220 and 2 000 cm^{-1} for CoO(OH). [b] Prepared by thermal decomposition of CoO(OH) at the indicated temperature. [c] J. Preudhomme and P. Tarte, *Spectrochim. Acta, Part A*, 1971, **27**, 1817.

TABLE 3

Rate constants for the decomposition of CoO(OH)

θ_c/°C	$k_{obs.}/s^{-1}$ [a]	Intercept [b]	m [c]	E_a/kJ mol^{-1}	$k_{obs.}/s^{-1}$ [d]	E_a/kJ mol^{-1}
264	$(2.50 \pm 0.52) \times 10^{-5}$	1.03 ± 0.05	1.599 ± 0.24	205 ± 23	$(6.00 \pm 0.2) \times 10^{-5}$	214 ± 11
270	$(6.04 \pm 0.48) \times 10^{-5}$	1.08 ± 0.03	1.53 ± 0.05		$(1.00 \pm 0.08) \times 10^{-4}$	
275	$(6.09 \pm 0.22) \times 10^{-5}$	1.07 ± 0.012	1.50 ± 0.10		$(1.60 \pm 0.03) \times 10^{-4}$	
280	$(8.60 \pm 0.28) \times 10^{-5}$	1.04 ± 0.01	1.41 ± 0.04		$(2.00 \pm 0.06) \times 10^{-4}$	
291	$(2.66 \pm 0.05) \times 10^{-4}$	1.00 ± 0.01	1.35 ± 0.06		$(6.20 \pm 0.01) \times 10^{-4}$	
301	$(7.61 \pm 0.01) \times 10^{-4}$	1.00 ± 0.01	0.90 ± 0.10			
311	$(1.25 \pm 0.02) \times 10^{-3}$	1.04 ± 0.1	1.21 ± 0.10	101 ± 7		
321	$(1.50 \pm 0.05) \times 10^{-3}$	0.989 ± 0.01	1.00 ± 0.11			
341	$(2.76 \pm 0.10) \times 10^{-3}$	0.980 ± 0.15	1.12 ± 0.05			
361	$(7.13 \pm 0.20) \times 10^{-3}$	1.05 ± 0.02 [e]	1.10 ± 0.01 [e]			
391	0.0133 ± 0.001	[e]	[e]			

[a] From plots of $(1-\alpha)^{\frac{1}{2}}$ against time. [b] Intercept of plot of $(1-\alpha)^{\frac{1}{2}}$ against time. [c] Slope of plot of ln − [ln(1 − α)] against ln(time), $0.1 < \alpha < 0.5$. [d] From plots of $\sqrt[1.5]{-\ln(1-\alpha)}$ against time. [e] Large zero-time error invalidates intercept and m values.

models the reaction well. The activation energy calculated for this ' high-temperature phase ' of the decomposition is 101 ± 7 kJ mol^{-1}.

At temperatures below 290 °C the fit to rate law (2) becomes unacceptable (Table 3, Figure 2); in contrast to Avramov's [4] conclusions this suggests that a different rate law may be appropriate. If the poor fit to rate law (2) is accepted and the corresponding rate constants calculated (Table 1, Figure 3), a conventional analysis of their temperature dependence leads to an activation energy of 205 ± 23 kJ mol^{-1}, Figure 3, Table 3.

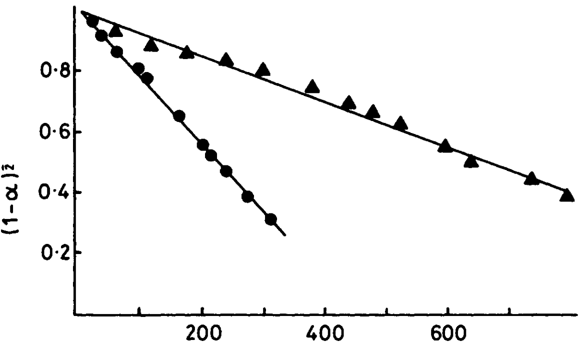

FIGURE 1 Plots of $(1-\alpha)^{\frac{1}{2}}$ against time for the decomposition of CoO(OH) at 341 (●) and 301 °C (▲) [for (●) the horizontal axis represents 2.5t]

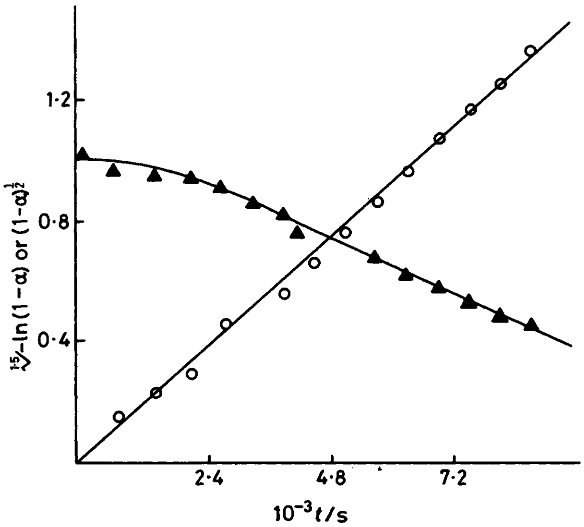

FIGURE 2 Comparison of kinetic laws for decomposition of CoO(OH) at 275 °C: $\sqrt[1.5]{-\ln(1-\alpha)}$ (○); $(1-\alpha)^{\frac{1}{2}}$ (▲)

The choice of an appropriate rate law for the low-temperature region was made on the basis of the formal kinetics of the system. The use of plots in ln − [ln(1 − α)] against ln$t$ to analyse kinetic data has been discussed; [8] slopes close to unity (0.1 < α < 0.5) indicate that the concept of an order of reaction is appropriate. At low temperatures the slope of such plots becomes *ca.* 1.5 (Table 3) whether for the range 0.1 < α < 0.5 or for 0.1 < α < 0.9.

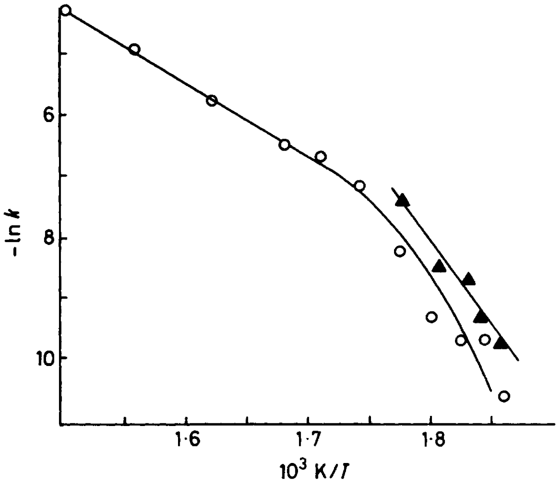

FIGURE 3 Arrhenius-type plot for the decomposition of CoO(OH): rates from $\sqrt[1.5]{-\ln(1-\alpha)}$ (○) and from $(1-\alpha)^{\frac{1}{2}}$ (▲)

This slope of 1.5 empirically suggests that an equation of type (3) might model the kinetics. Non-integral values of

$$\sqrt[1.5]{-\ln(1-\alpha)} = kt \qquad (3)$$

the index in kinetic models of this (Avrami–Erofeyer) type are controversial; Young [10] holds them to be meaningless while Hulbert [11] suggests they may be justified. Equation (3) fits well our data in the low-temperature region, little difference being made to the activation energy if the Avrami–Erofeyer equation with $n = 2$ is used. Conventional analysis of the rate constants obtained by this method leads to an activation energy of 214 ± 11 kJ mol^{-1} and the fit is much improved relative to that obtained from rate constants calculated using equation (2), see Table 3 and Figure 3.

Heterogenite.—A preliminary study of the thermal decomposition of heterogenite (B.M. 1930, 980 [1]) was carried out. Thermogravimetric analysis of the sample (10 °C min^{-1}, 10 cm^3 N_2 min^{-1}) revealed a 1% loss in the region 50—150 °C and a 13% loss between 150 and 361 °C, in contrast to the theoretical value of 12.7% required for the decomposition of CoO(OH). The extra 1% mass loss was attributed to water occluded in the sample; this proved to be a major obstacle in the study of this mineral.

As reported by Avramov,[4] even such a small quantity of water has an enormous effect on the isothermal kinetics. The first 20—40% of the reaction occurs very rapidly, presumably due to the disruption of the crystal structure as this water escapes. Subsequent to this initial mass loss, rate law (2) is obeyed. Analysis of the rate constants obtained from rate law (2) between 270 and 380 °C leads to an activation energy of 109 ± 20 kJ mol^{-1}. Infrared and diffraction studies of both product and reactant give similar results to those obtained for synthetic CoO(OH), although both materials were less crystalline than the corresponding synthetic species. The kinetic data are summarised in Table 4.

TABLE 4

Kinetic results for the decomposition of heterogenite

θ_c/°C	$10^4k/\text{s}^{-1}$	E_a/kJ mol^{-1}
270	2.27	
331	28.7	109 ± 20
361	71.4	
381	131	

DISCUSSION

In contrast to the results of Avramov,[4] we find that a change of mechanism occurs at *ca.* 290 °C. The decomposition of CoO(OH) above 290 °C is well described by phase-boundary control in two dimensions; below this temperature nucleation and growth kinetics more accurately describe the decomposition.

The activation energy obtained for the high-temperature decomposition compares well with that of similar reactions [γ-FeO(OH) [12] 125 kJ mol^{-1}, $Co(OH)_2$ [13] 93 kJ mol^{-1}] although our value is somewhat higher than the 79 kJ mol^{-1} reported by Avramov. Only two temperatures below 290 °C are reported by this author; it is therefore possible that a value close to 100 kJ mol^{-1} for the high-temperature region is consistent with Avramov's results.

The rate law used for the low-temperature phase of the decomposition is empirically consistent with the results. The Avrami–Erofeyer equation with $n = 2$ is an alternative possible description of the kinetics. The latter leads to a similar activation energy while preserving the two-dimensional symmetry of the reaction.

The decomposition of heterogenite proceeds with an activation energy within experimental error of that obtained for the high-temperature phase of CoO(OH) decomposition.

EXPERIMENTAL

The compound CoO(OH) was prepared by the method of Ibers and co-workers,[2] and oven dried at 100 °C for 12 h. A sample of heterogenite was kindly supplied by the British Museum (Natural History). It was carefully picked to be free of pseudomalachite as described by Hey.[1]

Methods.—Infrared spectra were recorded for Nujol mulls between CsI plates in the range 250—3 500 cm^{-1} using a Perkin-Elmer 257 spectrophotometer. *X*-Ray powder photographs were obtained by the Debye–Scherrer method using Cu-K_α radiation. Thermogravimetric analysis was performed under nitrogen (10 cm^3 min^{-1}) using a Stanton Redcroft TG-750 at 10 or 5 °C min^{-1}, the sample size being in the range 6—10 mg. In experiments on isothermal weight loss, the sample was plunged into the furnace preheated to the required temperature, to minimise errors due to equilibration. The temperature was recorded with a Pt–Pt,Rh(13%) thermocouple with ice–water as reference.

Rate constants and activation parameters were calculated by least-squares procedures; reported errors are one standard deviation in the case of synthetic CoO(OH). Due to the additional difficulties inherent in the study of heterogenite, errors are *estimated* as at least 15% for these results.

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