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SOLID-SOLID REACTION OF CADMIUM OXIDE AND SILVER SULFATE

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ABSTRACT

The chemistry and the kinetics of the reaction of cadmium oxide and silver sulfate is reported. The reaction in the solid state was performed at 500, 540, 570, 600 and 630°C. The products were oxygen, cadmium sulfate and metallic silver. The proposed mechanism suggests the formation of an intermediate silver oxide. The kinetics indicate that the reaction proceeds by a diffusion-controlled mechanism.

INTRODUCTION

The kinetics of solid–solid reactions is described by various equations [1]. All the equations can, however, be reduced to be based on three types of models [2]: (i) Diffusion models, where the rate is determined by material transport through the product layer; (ii) Phase boundary models, where the rate determining step is the chemical reaction at the phase boundary; (iii) Nuclei growth models, where the rate determining step is the growth of the products phase from randomly distributed nuclei. In the present communication the reaction of solid cadmium oxide and solid silver sulfate is reported. To the best of the authors' knowledge this reaction was not studied previously. The chemistry of the reaction will be described and a preliminary kinetic analysis will be presented.

EXPERIMENTAL

The preparation of the reactants

Cadmium(II) oxide

This was prepared by heating cadmium carbonate (BDH Analar) in air at

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[†] Deceased.

600°C for 10 hours. The non-stoichiometric brownish oxide obtained was sieved and the 160 mesh fraction was used for the solid-solid reactions.

Silver sulfate

BDH AnalaR grade silver sulfate was dissolved in concentrated sulfuric acid (50%). The warm solution was put aside in the dark for recrystallization. The crystals formed while cooling (with stirring to prevent the growth of dendrites) were rinsed with cold, triple-distilled water (TDW). In order to obtain spherical particles the crystals were immersed in cold TDW and stirred at a constant velocity. The crystals so obtained were rinsed after separation from the mother liquor. The crystals had a shape between spheroids and spheres, as observed with a microscope. The interferences (polarizing microscope) for each crystal were continuous, showing the absence of twins or aggregates of microcrystals. The 60–80 mesh fraction was used for the reaction.

The reactors and vacuum lines were as described previously [3].

RESULTS

The stability and behavior of the reactants by heating in vacuum were surveyed.

Cadmium oxide

It was realized that the weight-loss properties of the oxide depended on its history.

Fresh cadmium oxide

Samples weighing around 100 mg were heated subsequent to their preparation at 600°C in vacuum (initial pressure 10^{-5} Torr). A silvery mirror of metallic cadmium was deposited on the cold walls of the reactor. Simultaneously, the oxygen pressure was elevated and a weight loss was recorded with a Chan balance. Naturally, the weight loss calculated from the oxygen evolved was lower because of the evaporated cadmium. A similar behavior was observed for a freshly prepared cadmium oxide sample kept in a desiccator for two days.

Aged cadmium oxide

A sample was kept in a vacuum desiccator for four months. The heating treatment as described above resulted in a negligible pressure elevation (0.7 μm). Also, no metal was deposited on the cold walls.

For the solid–solid reaction the aged cadmium oxide was used.

Silver sulfate

The salt was not decomposed by heating in vacuum to 600°C.

Preliminary reactions

A mixture of cadmium oxide (1 g, 7.8×10^{-3} mol) and silver sulfate (1 g, 3.2×10^{-3} mol) was ground in an agate mortar in a glove box. The mixture was evacuated at room temperature for 1 h at 10^{-5} Torr and was heated (without pumping) at 300°C for an additional 1 h. No pressure was developed during the heating. The sample was then heated for 20 min at 600°C and the reaction was terminated by removing the furnace. The reaction was not completed after this lapse of time (Fig. 1). The residue was not dissolved completely in TDW. The soluble part contained silver, cadmium and sulfates. Qualitative runs showed that the insoluble part contained cadmium oxide and metallic silver (was not extracted with ammonia showing that it is not silver oxide). For the analytical determination the insoluble residue was dissolved in concentrated nitric acid. Silver was determined by a potentiometric titration with hydrochloric acid. Cadmium was determined by EDTA titrations. The sulfate anion was determined by precipitation with barium chloride. A fairly good agreement was obtained between the calculated mass of the oxygen evolved in this incomplete reaction. The number of moles of oxygen and the silver present in the insoluble product were 2.2548×10^{-3} and 2.308×10^{-3}, respectively. Additional experiments are represented in Table 1. The results of a parallel experiment on the interdependence of

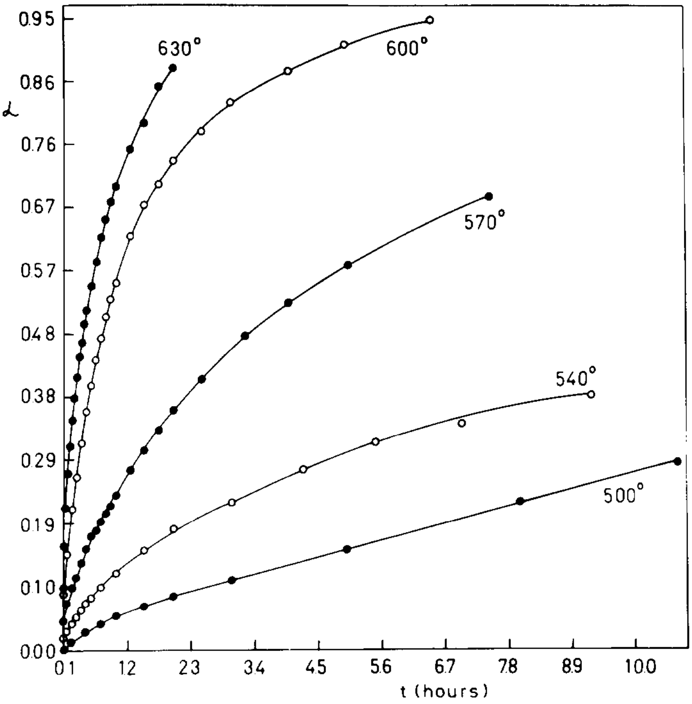

Fig. 1. Evaluation of oxygen.

cadmium, silver metal and sulfate are presented in Table 2. It can be realized that there is a good agreement between the number of moles of soluble cadmium and insoluble silver.

Reaction mixtures

To ensure that all the spherical particles of silver sulfate are fully embedded in cadmium oxide, mixtures were prepared having a formula weight ratio of 1 : 5, respectively. The mixture was passed five times through a 30-mesh sieve in order to homogenize the mixture. Samples weighing around 300 mg were used for the reactions. The developments of the reactions at various temperatures are presented in Fig. 1. In order to obtain reproducible results the mixtures were always preheated in vacuum at 300°C for 90 min. At this temperature no reaction was observed.

The solid–solid reactions were performed at five temperatures: 500, 540, 570, 600 and 630°C. The molar ratio of the reactants silver sulfate to cadmium oxide was 1 : 5, i.e., an excess of cadmium oxide.

The progress of the reaction was followed by a continuous recording of oxygen pressures. At the end of the reaction, analytical determinations were performed on the residues.

For the reactions at low temperatures the silver was determined by atomic absorption. The results are represented in Table 3. There is a fairly good agreement between oxygen and the silver sulfate which reacted at the temperatures 570, 600 and 630°C. At 500 and 540°C the agreement is rather poor, presumably because of the low amounts of silver in the insoluble residues.

TABLE 1

Measured and calculated oxygen pressures

Weight of mixture (mg)	Mole ratio CdO/Ag_2SO_4	Reaction temp. (°C)	Oxygen pressure (μm)	
			Measured	Calculated
241.4	4.4:1	614 (31 h)	268	261
394.4	4.4 :1	566 (9 h)	424	426

TABLE 2

Analyses of reaction products at 600°C (20 min) ($mol \times 10^{-3}$)

Reaction mixture		Cadmium		Silver sulfate from	
CdO	Ag_2SO_4	Soluble	Insoluble	Soluble	Insoluble
8.05	3.22	1.73	6.23	1.43	1.75

The X-ray diffraction studies carried out on the residues did not show the patterns of cadmium sulfate and metallic silver.

DISCUSSION

Solid silver sulfate reacted with solid cadmium oxide in the solid state. The reaction was of the type

$$\text{solid}_{(1)} + \text{solid}_{(2)} = \text{solid}_{(3)} + \text{gas} \qquad (1)$$

The gaseous product was oxygen. It is proposed that the solid products are cadmium sulfate and metallic silver in analogy to the reaction between silver sulfate and cadmium oxide [4]. The suggestion that one of the solid products is cadmium sulfate is based on the analytical results (Table 2).

Accordingly, the overall reaction will be described by

$$CdO_{(s)} + Ag_2SO_{4(s)} = CdSO_{4(s)} + 2Ag_{(s)} + \tfrac{1}{2}O_{2(g)} \qquad (2)$$

The amount of oxygen evolved by this reaction should then be equivalent to the insoluble silver formed. The analytical results confirm this (Table 3). On the other hand, the determinations of sulfate, cadmium and soluble silver support the assumption that the soluble cadmium appears as the sulfate. From Table 2 we see that the insoluble silver is equivalent to the soluble cadmium supporting a reaction described by eqn. (2). The possibility that oxygen originated from the thermal decomposition of cadmium oxide or from the decomposition of sulfates is not plausible. This conclusion is based on: (i) the blank experiments of heating aged cadmium oxide and silver sulfate at the reaction temperatures (as for cadmium sulfate it is stable at these temperatures [5]); (ii) the total amount of sulfate anion does not change during the reaction (Table 2). Also, qualitative tests for acidities in the cooled traps did not show the presence of a compound showing acidity when dissolved in water, i.e., no sulfur oxides were present.

The reason that silver and cadmium sulfate were not observed by X-ray

TABLE 3

Comparison of reaction products

Temp. (°C)	Measured O_2 pressure (μm)	Calc. O_2 pressure from measured pressure + insoluble silver	Calc. O_2 pressure from initial silver sulfate
500	176.9	274.5	322.4
540	121.1	182.6	312.2
570	221.4	341.4	324.0
600	280	340	308.4
630	287	334.5	326.9

diffraction may be because of dispersion of the small crystallites formed.

It seems quite possible that silver oxide (Ag_2O) is an intermediate formed by double decomposition:

$$CdO_{(s)} + Ag_2SO_4 = CdSO_{4(s)} + Ag_2O_{(s)} \tag{3}$$

The silver oxide is not stable and decomposes between 160 and 250°C.

From DTA experiments carried out in this laboratory [6] it was found that silver oxide decomposed (in ambient air) at 400°C, possibly because of a kinetic delay as found by Lewis [7] in his classical work.

In the presence of silver sulfate the decomposition of silver oxide was somewhat delayed to 420°C [6]. These results and the literature information may indicate that if silver oxide is an intermediate compound it decomposes at the reaction temperatures. The proposed silver oxide intermediate could not be isolated because the reaction between silver sulfate and cadmium oxide took place at higher temperatures whence it decomposes. The absence of an induction period may indicate that the intermediate Ag_2O decomposes instantaneously.

Kinetics

The development of the reaction was presented (Fig. 1) as α vs. time. ($\alpha = P_t/P_\infty$, where P_t is the normalized pressure of oxygen at time t and P_∞ is the pressure calculated for a complete reaction from eqn. (2)). The results were mathematically analysed with the use of a CDC 6000 computer and fourteen equations [2] were analyzed. The kinetic data for this reaction correspond well with the Jander equation [2]

$$k_J t = \frac{2kDt}{r_0^2} = \left[1 - (1-\alpha)^{1/3}\right]^2$$

where k_J is the rate constant, k is a proportionality constant, t is the time, D is the diffusion coefficient, r_0 is the initial radius of the reacting particles, and $\alpha = P_t/P_\infty$. From Fig. 2 we see that a linear dependence is obeyed for the low temperature runs, i.e., 500 and 540°C. For the higher temperatures a deviation is observed after a longer reaction time. It is proposed that this deviation is a result of changing the diffusion coefficient, D. At lower temperatures the extent of the reaction is low so that the product layer formed does not inhibit diffusion and D is constant. With the progress of time the product layer on the spheres (or spheroids) is thicker and changes may occur that effect the constancy of D. The apparent activation energy calculated was 223.4 kJ mol^{-1}. It should be emphasized here that no intention of assigning a mechanism based on the obeying of a kinetic reaction is proposed. Further work on the reaction with isotopically labeled $Cd^{18}O$ is needed.

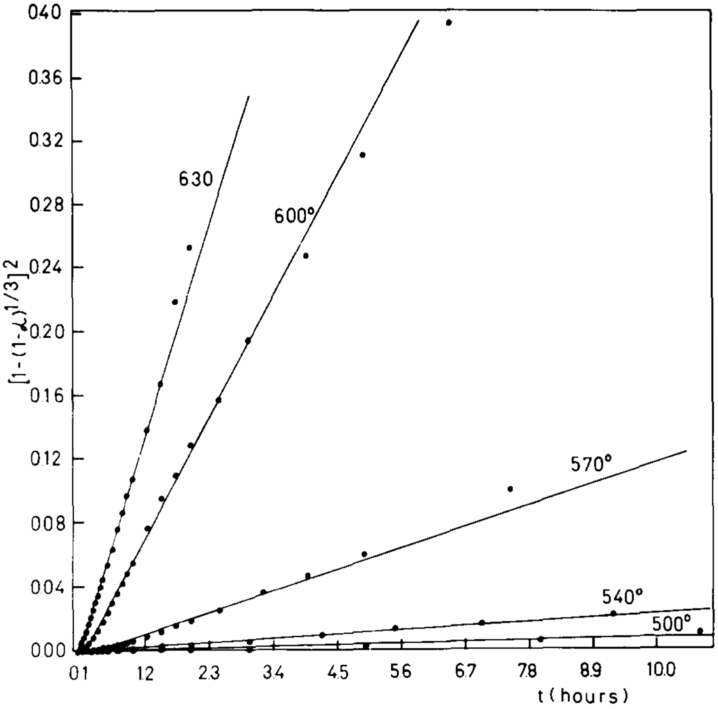

Fig. 2. Description of the reaction by the Jander equation.

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