

Mechanism of the Powder Reaction between $\text{CuSO}_4(\text{s})$ and PbO (α and β): A Thermoanalytical and Mass Spectrometric Study

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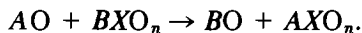
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Thermoanalytical studies and isotopic analysis of oxygen have been used to establish the actual mechanism of the $\text{CuSO}_4/(\alpha,\beta)\text{PbO}$ 1/1 *M* exchange reaction (the reactants are fine powders). Whether SO_3 is or is not involved in the reaction process depends on the crystalline form of PbO , and in the case of α - PbO on the type of heating. Oxygen isotope analysis, carried out on reaction products when PbO is enriched in ^{18}O and when gaseous SO_3 does not play any part in the process, shows that both cationic and oxygen transport are involved in the reaction mechanism.

Introduction

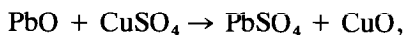
The reaction studied here belongs to the type of reactions between oxides and oxisalts, discovered by Hedvall and Heuberger (1), and correspond to the general formula:



These solid-state reactions have been named exchange reactions and they occur at temperatures lower than the dissociation temperature of either of the reactants. However, when the difference between reaction and dissociation temperature is small, doubt arises about whether the reaction mechanism between these two solids

proceeds by gas or ionic solid–solid transport. This point has caused great controversy over the real mechanism of these exchange reactions.

The exchange reaction being considered in this paper:



is illustrative of this kind of controversy. For example, Tammann (2) established that this reaction is a solid–solid process, since the exchange reaction takes place between 495 and 700°C, whereas, according to Hedvall (3), the CuSO_4 decomposition starts at 660°C. On the other hand, Pozin *et al.* (4) investigated the reaction as a function of pressure and found, under isothermal (500°C) conditions, the reaction degree decreased with pressure. Furthermore, they observed that the reaction degree is the same in the presence or in the absence of an inert powder (Al_2O_3 or SiO_2) (5). They hypothesized from these results that PbSO_4

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formation was gas transport (SO_3) controlled.

In light of these findings it seemed interesting to study this reaction by thermoanalytical techniques and in a vacuum furnace (6). Since neither of the above authors reported the crystalline form (α or β) of PbO , both forms were used here. The objective is to show whether or not the reaction involves SO_3 and, if it does not, whether the reaction mechanism is characterized only by cationic transport in the reaction layer or whether oxygen ion transport is involved as well. The most suitable method to clarify this last point is to use PbO enriched with ^{18}O and to measure the oxygen isotope ratio in the products of the reaction. This can be done by separating the two products of the reaction, CuO , PbSO_4 , and converting the oxygen to CO_2 . A mass spectrometer can then be used to measure easily the ^{18}O levels in the liberated CO_2 .

Experimental

Materials

All starting materials used for chemical preparations were reagent grade. CuSO_4 was obtained by heating the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to 300°C . β - PbO and α - PbO were prepared as previously described (7, 8). Labeled β - PbO containing 5.68–6.01% of ^{18}O was obtained by mixing Miles-Seravac's β - PbO . Pure CO and Ar (99.995%) were used for reduction and inert atmosphere control, respectively. Equal molar mechanical mixtures of CuSO_4/α - PbO or β - PbO were used in these experiments.

Methods

DTA recordings were performed using an apparatus designed in this laboratory, with sintered alumina holders and chromel/alumel differential thermocouple, incorporating junctions inside the sample and reference; α - Al_2O_3 was used as refer-

ence. Samples were heated in air atmosphere at $150^\circ\text{C}/\text{h}$ and $300^\circ\text{C}/\text{h}$.

Thermogravimetric experiments were performed with a Chevenard Thermobalance, model No. 39, equipped with an Adamel vertical furnace and a photographic recording device. Samples of about 300 mg were placed in porcelain crucibles and air-heated at the rate of $300^\circ\text{C}/\text{h}$.

X-Ray powder diffraction served for structural characterization of reaction products when the powder reactant mixture is heated at different temperatures. Random powder samples were analyzed on an X-ray Philips diffractometer using $\text{CuK}\alpha$ radiation and a Ni filter.

In order to determine SO_3 involvement in the reaction process, the powder reactant mixture was heated in a vacuum furnace. This device is similar to the one designed by Burriel and García-Clavel (6), but made of materials suitable for higher temperatures. Powder samples (500 mg) were placed as a 2-mm-thick layer on the bottom of a porcelain filtering microcrucible. In this method, a strong stream of either air or Ar gas is passed through the sample and porous bottom of the crucible during heating. If decomposition of CuSO_4 occurs before reaction, the evolved gas would be partially removed before it has time to react. By analysis of SO_3 content on heated samples it is possible to determine whether the reaction mechanism is either solid–solid or gas solid.

Mass spectrometric studies were performed by means of a Consolidated Electroynamics Corp. model 21-103 C mass spectrometer for gaseous samples, equipped with an electron bombardment ion source of 70 eV and 250°C . An ionizing current of $10 \mu\text{A}$ was used. The pressure of the sample, measured with a micromanometer, ranged from 20 to 100μ . The region of the spectrum used for calculation is one corresponding to CO_2^+ ions.

CuSO_4/β - Pb^{18}O exchange reaction was

carried out in the same type of microcrucible used in the vacuum furnace method (equal molar solid mixtures totaling 250 mg of $\text{CuSO}_4/\beta\text{-PbO}$ were used) inside a Pyrex glass bulb. When vacuum levels better than 0.1μ were obtained in the bulb, sufficient argon gas was introduced to attain pressures close to ambient (500°C). The bulb was heated at a rate of $150^\circ\text{C}/\text{h}$ up to 500°C and kept at this temperature for 5 hr.

To separate the reaction products, CuO and PbSO_4 , the reacted mass was divided into two aliquots, in one of them, CuO is removed; in the other, PbSO_4 . To eliminate CuO , the solid is dissolved in HNO_3 (conc.) and then PbSO_4 is precipitated from solution by adding ethyl alcohol. After filtration, the PbSO_4 precipitate was rinsed with distilled water until the wash liquid was free of NO_3^- . Drying operations were carried out under vacuum at room temperature. The second aliquot of the reacted mass was treated with 3 M NaNO_2 aqueous solution, which dissolves PbSO_4 (9). The CuO was washed, first with NaNO_2 solution and then with distilled water until the wash liquid showed no reaction with Griess reagent. Spectroscopic analysis of this copper oxide gave a Pb content smaller than 0.1%.

The reduction reactions of PbSO_4 and CuO were carried out in Pyrex glass bulbs using carbon black and CsCl (as a catalyst) to reduce PbSO_4 , pure carbon monoxide was used to reduce CuO . Vacuum better than $0.1 M$ was obtained in both the bulb containing PbSO_4 with carbon (C) as the reductant and the one with CuO , which was later filled with CO as the reductant. The bulbs were then flame sealed. Bulbs containing CO_2 , produced in the reaction, were

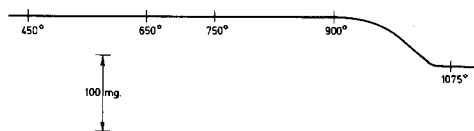


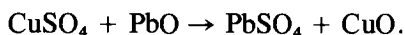
FIG. 1. TG curve of CuSO_4/PbO (α and β), weight of sample 298 mg.

attached to the mass spectrometer inlet system. These were then broken with a magnetic hammer allowing the gas to escape to the spectrometer.

Results and Discussion

Thermogravimetric Analysis

The recorded thermogravimetric curve in air, Fig. 1, for mixtures of CuSO_4 with either β - or α - PbO is a horizontal line from room temperature to 900°C . Decomposition then sets in abruptly and continues to 1075°C . The weight loss at this temperature corresponds to a higher value than would otherwise be measured if the loss were due solely to SO_3 . The additional loss of weight is due to the inevitable disappearance of oxygen from CuO that starts above 1050°C (10). The loss of SO_3 can occur either as a result of CuSO_4 or PbSO_4 decomposition. Since the temperature range for which the loss of weight appears coincides with PbSO_4 and not CuSO_4 decomposition, this reveals that the powdered mixture has reacted previously, most probably according to the exchange reaction,



Unfortunately, thermogravimetric analysis cannot show the temperature at which this reaction takes place, since it occurs without a change in mass.

Differential Thermal Analysis

DTA curves of both $\text{CuSO}_4/\alpha\text{-PbO}$ and $\text{CuSO}_4/\beta\text{-PbO}$ mixtures are given in Figs. 2a-d. When $\text{CuSO}_4/\alpha\text{-PbO}$ sample is heated at $300^\circ\text{C}/\text{hr}$, the DTA curve shows a large exothermic peak in the range $500\text{--}720^\circ\text{C}$, with a step between 575 and 600°C (Fig. 2a). The X-ray diffraction pattern of the residue at 750°C shows the presence of CuO and PbSO_4 . Therefore, this peak can be attributed to the exchange reaction between these solids, which is exothermic, as

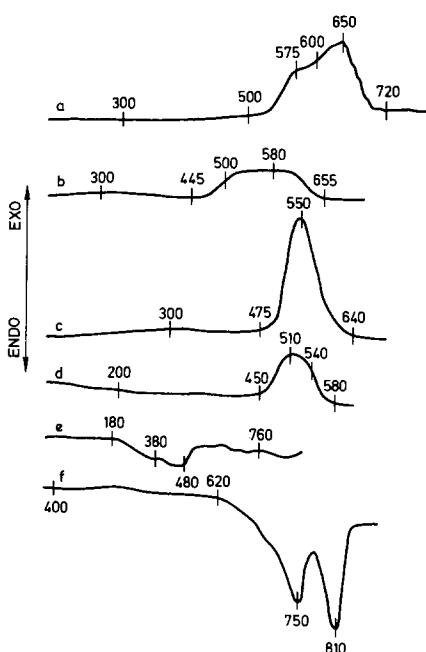


FIG. 2. DTA curves: (a) $\text{CuSO}_4/\alpha\text{-PbO}$ 1/1M; $v = 300^\circ\text{C/hr}$; (b) $\text{CuSO}_4/\alpha\text{-PbO}$ 1/1M, $v = 150^\circ\text{C/hr}$; (c) $\text{CuSO}_4/\beta\text{-PbO}$ 1/1M, $v = 300^\circ\text{C/hr}$; (d) $\text{CuSO}_4/\beta\text{-PbO}$ 1/1M, $v = 150^\circ\text{C/hr}$; (e) PbSO_4/PbO 1/1M, $v = 300^\circ\text{C/hr}$; (f) CuSO_4 , $v = 300^\circ\text{C/hr}$.

one would expect for a solid–solid reaction (11).

In order to determine the reaction pathway, X-ray diffraction patterns of residues at 580 and 625°C were also obtained. These patterns show the presence of the reactants CuSO_4 and $\alpha\text{-PbO}$ as well as final products PbSO_4 , CuO , and $\text{PbSO}_4 \cdot \text{PbO}$. At 625°C, on the other hand, PbSO_4 , CuO , and $\text{PbSO}_4 \cdot \text{PbO}$ are the only compounds identified. Since $\text{PbSO}_4 \cdot \text{PbO}$ requires a contribution of SO_3 to transform PbO into PbSO_4 and CuSO_4 was not detected, gaseous SO_3 may exist in the reaction mass. The reaction between PbO and PbSO_4 to form $\text{PbSO}_4 \cdot \text{PbO}$ is endothermic (12, 13) (see Fig. 2e) and takes place at lower temperatures (180–480°C) than the exchange reaction (480°C). Furthermore, CuSO_4 starts to decompose at 620°C, as is shown in Fig. 2f. Since the temperature at the

maximum of the exothermic peak is 650°C, this means that the exchange reaction has not yet finished when CuSO_4 decomposition starts. Therefore, the shape of the exothermic peak is due to overlapping of (a) the exchange reaction, (b) the formation of $\text{PbSO}_4 \cdot \text{PbO}$, and (c) the CuSO_4 decomposition.

The DTA curve obtained (Fig. 2b) using a lower heating rate (150°C/hr) shows a single broad exothermic peak between 445°C and 655°C. The amplitude is smaller than the one above (Fig. 2a) recorded at 300°C/hr, but is due to the well-known influence of heating rate on peak areas. The most meaningful differences between peaks in Figs. 2b and 2a are, first, the peak in Fig. 2b is shifted toward lower temperatures and, second, it does not show a shoulder. The end of the exchange reaction may occur before the start of the CuSO_4 decomposition (620°C, see Fig. 2f) since, according to Mackenzie (14), the end of this type of reaction must be between T_m (600°C) and the temperature at which the curve returns to base line (650°). The X-ray diffraction pattern of the residue appearing in Fig. 2b at 580°C shows, as before, the presence of $\text{PbSO}_4 \cdot \text{PbO}$ as a transitional compound of the exchange reaction.

DTA curves corresponding to $\beta\text{-PbO}$ mixtures with CuSO_4 appear in Figs. 2c and d corresponding to the two different heating rates employed. Note that sharper signals are produced with $\beta\text{-PbO}$ (Figs. 2a–2b) than with its α analog. This exothermic peak becomes smaller and shifts to 510°C (T_m) when the sample is heated more slowly (Fig. 2d). In both of these cases X-ray diffraction examination of samples heated before the peak temperature did not give any evidence for $\text{PbSO}_4 \cdot \text{PbO}$. This is probably due to the greater reactivity of $\beta\text{-PbO}$.

Vacuum Furnace

Table I shows that in the case of the

TABLE I^a
 SO_3 CONTENT (mg) IN 100 mg OF SAMPLE HEATED TO 750°C

Atmosphere	$\text{CuSO}_4/\alpha\text{-PbO}$		$\text{CuSO}_4/\beta\text{-PbO}$	
	300°C/hr	150°C/hr	300°C/hr	150°C/hr
With a stream of air passing through the sample	18.4	20.9	21.2	21.4
	19.9	21.3	20.9	21.2
	17.7	21.2	21.0	21.0
Static open air ^b atmosphere	21.4	—	21.0	—
	21.2	—	21.1	—
	21.2	—	21.3	—

^a Triplicate samples.

^b Theoretical content.

$\text{CuSO}_4/\alpha\text{-PbO}$ mixture, heated at 300°C/hr with air passing through the sample, the SO_3 content in the residue is smaller than in the unheated mixture (theoretical value) and differs from one experiment to another. This means that the stream of air has removed a portion of the SO_3 from the sample during heating. In contrast, all the rest of the experiments show the content of SO_3 to be the same in unheated and in heated samples. Furthermore, the reproducibility in the first case at 300°C with $\alpha\text{-PbO}$ is easy to understand since the rate of air flow was not the same for all three experiments.

The combination of DTA results and those shown in Table I demonstrates that gaseous SO_3 may or may not play a role in the reaction depending on the reactivity of the PbO , which in our experiments was directly related to the crystallographic form and, in the case of the $\alpha\text{-PbO}$, also with the type of heating of the powder mixture. It can be hypothesized that the gaseous product is formed if the combination of the above-mentioned variables is such that the exchange reaction is not complete before the CuSO_4 decomposition starts.

Isotopic Analysis of Oxygen in the Products of the Reaction

It has been experimentally established that Pb^{18}O exchanges oxygen with the air

when the mixture $\text{CuSO}_4/\text{Pb}^{18}\text{O}$ is heated in an open atmosphere (15). Therefore, the mixture was heated in an Ar atmosphere in order to perform isotopic analysis of these reactions. One has to additionally consider that the atmosphere has a substantial effect on reactions in which gases are liberated. Thermodynamically, a reaction giving a gaseous product, such as the thermal decomposition of the CuSO_4 ($2\text{SO}_3 \rightarrow 2\text{SO}_2 + \text{O}_2$), which occurs in a gaseous medium with a given partial pressure of this gas (O_2), occurs only when the dissociation pressure of the decomposition reaction corresponds to the partial pressure of the gas or exceeds it. The effect of using Ar instead of air is to decrease the partial pressure of O_2 , thus shifting the CuSO_4 dissociation temperature to lower values. It was therefore necessary to determine the choice of the experimental heating conditions under which the exchangeable reaction is finished, such that gaseous SO_3 was not released in the process. In order to determine these conditions, isothermal decomposition curves of CuSO_4 in Ar were recorded at different temperatures and the exchange reaction carried out in Ar stream using the vacuum furnace. From these experiments it has been established that in Ar the mixture should be heated at 150°C/hr to 500°C, and kept at this temperature for 5 hr

TABLE II
ISOTOPIC ANALYSIS OF OXYGEN ON THE PRODUCTS OF THE REACTION
BETWEEN CuSO_4 AND $\beta\text{-PbO}$ IN Ar ATMOSPHERE

Expt.	Compound	Intensities of the peaks of mass			$\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right) \text{CO}_2$	Percentage of marked molecules
		44	45	46		
1	PbSO_4	887.0	10.5	20.2	0.0114	3.70
	CuO	1255.0	14.6	23.7	0.00944	1.47
2	PbSO_4	464.9	5.6	8.4	0.00905	2.77
	CuO	1238.5	14.4	20.85	0.00842	1.39

for a sample weight of 250 mg.

Under this set of conditions, labeled oxygen was used to study the $\beta\text{-PbO-CuSO}_4$ exchange reaction. Table II shows the results obtained. It can be seen in the column representing percentage of labeled molecules from CuO and PbSO_4 obtained in the exchange reaction that the oxygen label from PbO followed two directions appearing in both CuO and PbSO_4 because both reaction products clearly show an enrichment in ^{18}O (the normal isotopic oxygen composition should be $^{18}\text{O}/^{16}\text{O} = 0.00204$). Because gas phase (SO_3) control has been eliminated here, the only possible way to explain the presence of ^{18}O in PbSO_4 is to evoke an oxygen ion transport mechanism. The mechanism of ^{18}O incorporation can be interpreted in terms of the CuSO_4 structure (16). Here, every Cu atom is surrounded by oxygen atoms, each anion occupying the vertices of a very distorted Cu^{2+} octahedron. A distortion therefore also exists in the SO_4 tetrahedra and these distortions combined with the great increase of atomic vibrations due to temperature cause S-O bonds to break (the longest one more easily) and rearrange themselves with an ^{18}O from PbO , forming PbSO_4 which has a lattice structure of regular tetrahedra with much higher thermal stability.

Conclusion

By studying the CuSO_4/PbO exchange reaction with thermoanalytical and vacuum furnace techniques and by reassuring the transfer of ^{18}O label from reactants to products, it has been possible to elucidate the mechanism of this reaction. It appears that SO_3 involvement in this reaction depends on the crystalline form of PbO and in the case of $\alpha\text{-PbO}$ on the type of heating. For $\beta\text{-PbO}$, where SO_3 is not involved in reaction pathway, both cationic and oxygen transport are shown to be involved in the reaction mechanism. Previous controversies regarding gas or ionic solid-solid transport mechanisms can be understood in terms of a failure to control heating and/or solid phase reactivities in previous studies. It can be hypothesized that SO_3 is formed if the type of heating and/or solid reactivity is such that the exchange reaction is not complete before CuSO_4 decomposition starts.

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