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Effect of SO_2 on Chlorination of $Bi_2O_3 + Fe_2O_3$ Mixtures

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Abstract—The reaction of $Bi_2O_3 + Fe_2O_3$ mixtures with chlorine and SO_2 at 250–700°C is studied. At 300–500°C, the degree of bismuth chloride sublimation from the oxide mixture increases in the presence of SO_2. Chemical sublimation of $FeCl_3$ occurs after $BiCl_3$ is virtually completely recovered from the solid phase.

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Preparation of pure metal chlorides is an important problem of preparative inorganic chemistry. Chemical sublimation, which is transfer of the substance from a condensed to gaseous phase in the chloride form as a result of chemical reaction, is one promising method for selective separation of solid components [1].

Here, we report the study of reaction of Bi_2O_3 + Fe_2O_3 mixtures with chlorine in the presence of SO_2; this study was undertaken to find optimal parameters for $BiCl_3$ preparation from iron oxide mixtures. The importance of preparation of pure $BiCl_3$ arises from its wide use, in particular, in catalysis and as a precursor for metallic bismuth [2, 3]. Fe_2O_3 was shown to increase the Bi_2O_3 chlorination rate noticeably [4]. Addition of SO_2 to chlorine during chlorination of individual oxides increases the formation rates of bismuth and iron chlorides [5, 6].

To suggest the composition of reaction products, we calculated the equilibrium composition of the vapor and condensed phases in the Bi_2O_3–Fe_2O_3–Cl_2–SO_2 system with various component ratios. The basis for calculations was a variational technique; ASTRA software was used [7]. Figure 1a demonstrates partial pressure versus temperature for the vapor components of the Bi_2O_3–Fe_2O_3–$3Cl_2$–$3SO_2$ system; Figure 1b shows the composition of the condensed phase of this system. The temperature range 25–1000°C can be divided into two smaller ranges: a low-temperature range (up to 600°C) and high-temperature range (above 600°C). In the low-temperature range, iron in the condensed phase occurs as sulfate; most bismuth is trichloride and oxychloride. The overall process can be described as

$$Bi_2O_3 + Fe_2O_3 + 3Cl_2 + 3SO_2 = 2BiCl_3 + Fe_2(SO_4)_3, \quad (1)$$

$$Bi_2O_3 + Cl_2 = BiOCl + 1/2O_2. \quad (2)$$

A decrease in the chlorine proportion in the system does not increase the bismuth proportion contained in the oxychloride form in the condensed phase. $Fe_2(SO_4)_3$ is unstable at high temperatures; iron exists mostly as oxide. The vapor phase contains SO_2, SO_3, O_2, Cl_2, and iron chlorides in addition to $BiCl_3$; the iron chloride proportion is four orders of magnitude lower than the $BiCl_3$ proportion.

The considerable difference between the partial pressures of bismuth chloride and iron chloride implies that selective bismuth chloride sublimation is possible over a wide range of temperatures (250–1000°C).

EXPERIMENTAL

A flow-through technique [6] was used to study the reaction of $Bi_2O_3 + Fe_2O_3$ mixtures with chlorine and sulfur dioxide at 250–500°C. A weighed sample (0.6–0.9 g) was placed into a heated tubular reactor through which an inert gas was passed. After a set temperature was acquired, the inert gas was changed to the reaction gas. Volatile products were entrapped in cooled traps. The linear gas flow was 0.02 m/s.

The laws of chemical sublimation of metal chlorides at 550–750°C were studied gravimetrically on a setup with automated record of weight change [8]. The setup sensitivity was 0.001 g/mm scale. Sample sizes were 0.180–0.200 g. The overall gas consumption was 150–200 mL/min at a linear rate of 0.05 m/s. Under these conditions, the gas delivery rate to the surface did no control the process. Results were compared with relevant data on individual oxides.

Mechanical mixtures of high-purity grade bismuth oxide and iron oxide with various component ratios were used. Table 1 lists the compositions of these mixtures. X-ray powder diffraction and standard chemical analyses were used to characterize the starting samples and reaction products [9]. X-ray diffraction patterns were recorded on an ADP-2-01 diffractometer.

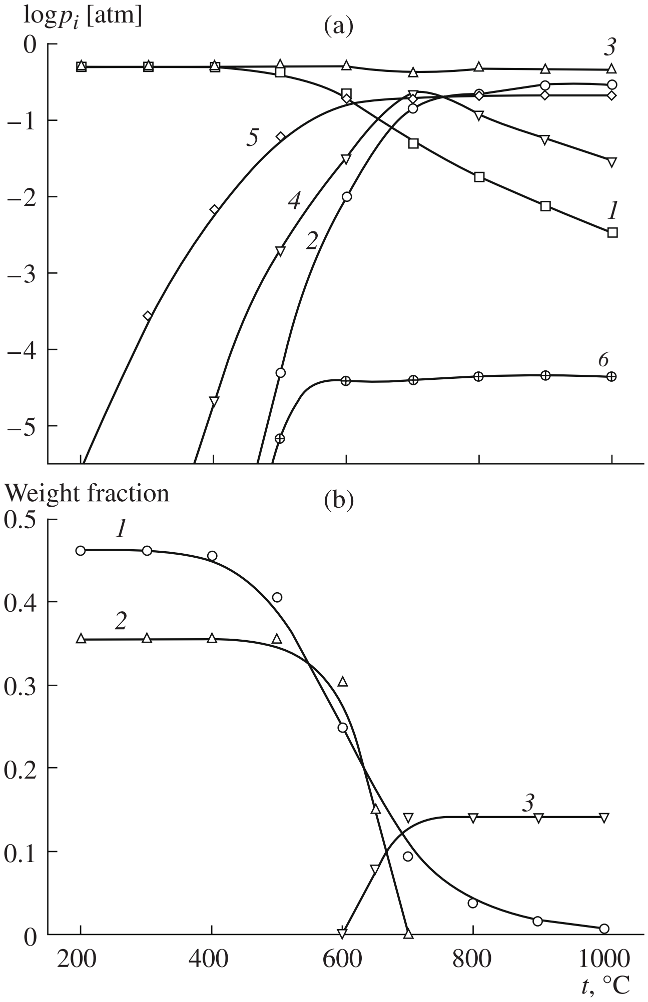

Fig. 1. Panel (a): equilibrium composition of the vapor phase of the Bi_2O_3–Fe_2O_3–$3Cl_2$–$3SO_2$ system: (*1*) Cl_2, (*2*) SO_2, (*3*) O_2, (*4*) SO_3, (*5*) $BiCl_3$, and (*6*) $FeCl_3$. Panel (b): the same for the condensed phase: (*1*) BiOCl, (*2*) $Fe_2(SO_4)_3$, and (*3*) Fe_2O_3.

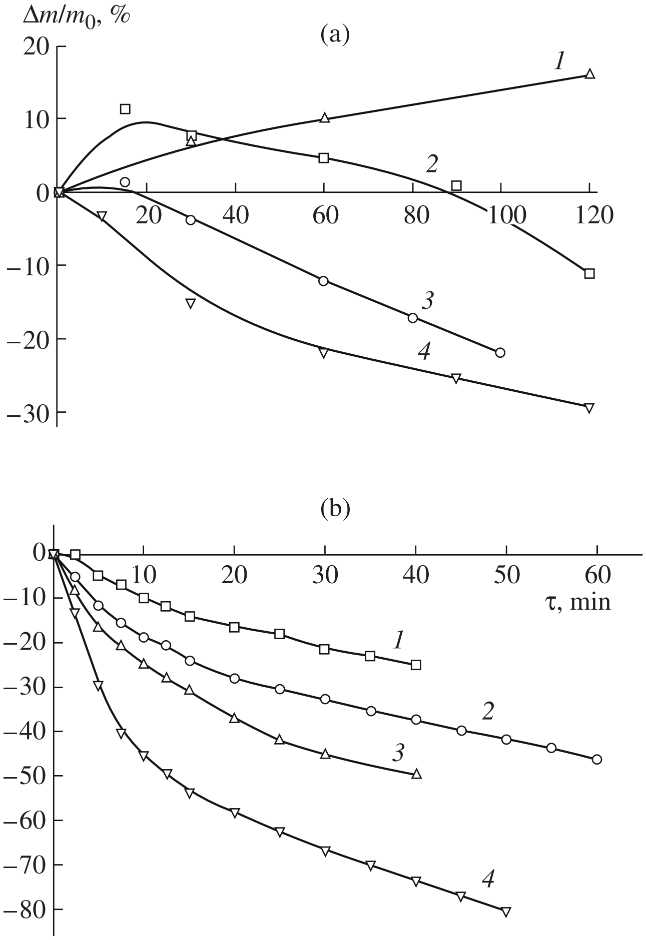

Fig. 2. Panel (a): isotherms for the reaction of Bi_2O_3 + Fe_2O_3 mixtures with Cl_2 + SO_2 (1 : 1 mol/mol) below 500°C: (*1*) 250, (*2*) 300, (*3*) 350, and (*4*) 400°C. Panel (b): the same above 500°C: (*1*) 550, (*2*) 600, (*3*) 650, and (*4*) 700°C.

RESULTS AND DISCUSSION

The reaction of Bi_2O_3 + Fe_2O_3 mixtures with chlorine in the presence of SO_2 has a noticeable rate even at 250°C and is accompanied by weight gain. At higher temperatures, the initial weight gain is followed by weight loss (Fig. 2a). The results of chemical and X-ray powder diffraction analyses imply that the initial weight gain during chlorination is due to the formation of bismuth oxychloride BiOCl and iron sulfate $Fe_2(SO_4)_3$ in the condensed phase. Subsequent weight loss is due to transfer of metal chlorides to the gas phase. Bismuth sulfate is not found in the solid phase, although its proportion is sufficiently high in the reaction of individual bismuth oxide with chlorine and sulfur dioxide [5].

Table 1 demonstrates how the degree of chemical sublimation of bismuth and iron trichlorides from mixtures their oxides of various compositions during chlorination in the presence of SO_2 at 400°C changes with time.

For bismuth oxide, degrees of chloride sublimation are low; they rise with increasing run duration to reach 12.5% for a contact time of 120 min. Addition of iron oxide to Bi_2O_3 considerably increases the degree of bismuth chloride sublimation. The degree of $BiCl_3$ chemical sublimation rises with increasing Fe_2O_3 proportion in the starting mixture. For a mixture containing 33.6% Fe_2O_3, the degree of bismuth chloride sublimation reaches 97.0% as soon as after 15 min. A further rise in Fe_2O_3 proportion insignificantly influences the degree of bismuth chloride sublimation. Complete bismuth chloride sublimation occurs under comparatively mild conditions: for example, at 400°C in 60-min runs for mixtures containing more than 23% Fe_2O_3, the bismuth proportion in the residue is less than 1%.

The iron chloride sublimation depends on the degree of $BiCl_3$ sublimation. If the degree of bismuth chloride sublimation does not exceed 60–70%, $FeCl_3$ chemical sublimation virtually does not occur. At high degrees of bismuth trichloride sublimation, the degree of iron chloride sublimation from mixtures increases considerably to approach the respective values for the individual oxide.

Table 2 displays the composition of chlorination products obtained from individual oxides and Bi_2O_3 + Fe_2O_3 (1 : 1 wt/wt) mixtures in the presence of SO_2.

According to previous data, mixtures the bismuth proportion transferred into sulfate in the reaction of Bi_2O_3 with $Cl_2 + SO_2$ is about 20% [5]. $Bi_2(SO_4)_3$ formation slows down the process. As a result, the degree of bismuth chloride sublimation at 300–450°C does not exceed 50%; the condensed phase contains $Bi_2(SO_4)_3$, BiOCl, and 8–15% of unreacted Bi_2O_3. In the presence of Fe_2O_3, the bismuth proportion bound into the trichloride increases dramatically. In the condensed phase, bismuth occurs exclusively as oxychloride; bismuth sulfate does not occur.

The degree of iron oxide conversion in chlorination of an oxide mixture in the presence of SO_2 is higher than for the individual oxide because of a considerable increase in the $Fe_2(SO_4)_3$ proportion. $FeCl_3$ formation is observed only for high degrees of bismuth chloride sublimation.

It was demonstrated previously [6] that the proportions of iron in chloride and sulfate are virtually the same in the reaction of Fe_2O_3 with a $Cl_2 + SO_2$ mixture; that is, $Fe_2(SO_4)_3$ is generated by the process described by the equation

$$2Fe_2O_3 + 3Cl_2 + 3SO_2 = Fe_2(SO_4)_3 + Fe_2Cl_6. \quad (3)$$

Iron sulfate accumulation decelerates chemical sublimation of iron trichloride.

In chlorination of Bi_2O_3 + Fe_2O_3 mixtures in the presence of SO_2, the iron fraction converted into sulfate is about two times that converted into chloride. The increased $Fe_2(SO_4)_3$ proportion in the condensed phase, the absence of $Bi_2(SO_4)_3$, and the increased degree of bismuth chloride sublimation within 250–450°C can arise from the fact that bismuth sulfate under the specified conditions is an intermediate. The increased degree of bismuth chloride sublimation results from the occurrence of the exchange reaction

$$Bi_2(SO_4)_3 + Fe_2Cl_6 = 2BiCl_3 + Fe_2(SO_4)_3. \quad (4)$$

The low thermal stability of $Bi_2(SO_4)_3$ [10] implies that the significance of reaction (4) will decrease at higher temperatures.

Table 1. Degree of $BiCl_3$ and $FeCl_3$ sublimation as a function of mixture composition (T = 400°C)

Mixture composition, %		τ, min	Percent chlorination	
Bi_2O_3	Fe_2O_3		Bi	Fe
100	0	15	4.0	–
		30	7.0	–
		60	10.6	–
		120	12.5	–
82.8	17.4	15	22.0	0.3
		30	39.7	0.5
		60	67.0	2.1
76.3	23.9	15	28.8	1.3
		30	87.3	13.4
		60	99.2	15.9
67.0	33.6	15	97.0	14.9
		30	98.8	26.6
		60	99.3	26.2
50.0	50.0	15	98.1	14.6
		30	98.7	25.7
		60	99.3	25.9
0	100	15	–	15.0
		30	–	25.6
		60	–	24.8

The results demonstrate that in cases where reactions rates are high and reaction products are stable in the reaction medium (iron sulfate), there is a clear correspondence between calculated and experimental data.

Figure 2b displays isotherms for chlorination of Bi_2O_3 + Fe_2O_3 mixtures in the presence of SO_2 at 550–700°C. An induction period is detected only at 550°C, unlike at low temperatures. A sublimate is formed immediately after the gas mixture is admitted to the reactor; it contains not only $BiCl_3$ but also $FeCl_3$. Even at 600°C, however, the solid residue contains sulfur;

Table 2. Composition of the products of reaction in Bi_2O_3, Fe_2O_3, and $Bi_2O_3 + Fe_2O_3$ mixtures (1 : 1 wt/wt) with $Cl_2 + SO_2$ mixture (1 : 1 mol/mol)

T, °C	τ, min	Bi distribution upon chlorination (percent of the starting)					
		$Bi_2O_3 + Fe_2O_3$		Bi_2O_3			
		$BiCl_3$	BiOCl	$BiCl_3$	BiOCl	$Bi_2(SO_4)_3$	Bi_2O_3
300	30	27.6	72.4	4.4	62.5	19.5	13.5
	60	66.7	33.3	7.4	58.1	20.2	14.3
	120	89.5	10.5	14.7	49.1	24.1	12.1
350	30	77.0	23.0	6.5	62.1	20.1	11.3
	60	95.9	4.1	8.6	60.3	21.2	9.9
400	30	98.7	1.3	7.0	66.7	18.9	7.4
	60	99.2	0.8	10.6	62.5	19.9	7.0
450	30	99.0	1.0	21.8	43.9	19.4	14.9
	60	99.1	0.9	34.4	32.4	20.5	12.7
600	30	99.2	0.8	–	–	–	–
650	30	99.3	0.7	–	–	–	–
		Fe distribution upon chlorination (percent of the starting)					
		$Bi_2O_3 + Fe_2O_3$			Fe_2O_3		
		$FeCl_3$	$Fe_2(SO_4)_3$	Fe_2O_3	$FeCl_3$	$Fe_2(SO_4)_3$	Fe_2O_3
300	60	24.1	47.2	38.7	23.7	22.8	53.5
350	60	22.4	57.2	15.8	24.8	24.3	50.9
400	60	24.2	57.6	18.4	24.8	22.3	52.9
450	30	26.5	47.6	25.9	24.6	20.3	55.2
600	60	31.4	47.7	20.9	–	–	–
650	60	48.6	2.7	49.6	–	–	–

this means that $Fe_2(SO_4)_3$ is formed. When the reaction time is 90 min, iron is completely transferred into the sublimate. This demonstrates that $Fe_2(SO_4)_3$ is an intermediate. At 650°C, the condensed phase is virtually free of sulfur (Table 2). The rate of $BiCl_3$ chemical sublimation considerably exceeds the $FeCl_3$ formation rate.

The bismuth chloride and iron chloride sublimation rates are considerably affected by the Cl_2 and SO_2 ratio in the vapor phase. Figure 3 displays the degree of metal chloride chemical sublimation as a function of Cl_2 and SO_2 ratio at 600°C. The degree of $BiCl_3$ chemical sublimation approaches 100% with SO_2 concentration increasing to 60%; a further increase in sulfur dioxide proportion brings about a decrease in the degree of $BiCl_3$ sublimation. For $FeCl_3$ chemical sublimation, this plot is a curve with a flat maximum, which is characteristic of conjugate reactions [1]. Similar curves were obtained previously [1, 6] in the chlorination of individual oxides (SnO_2, Sb_2O_4, Fe_2O_3) in the presence of SO_2. This means that the mutual influence of Bi_2O_3 and Fe_2O_3 during chlorination decreases in the high-tem-

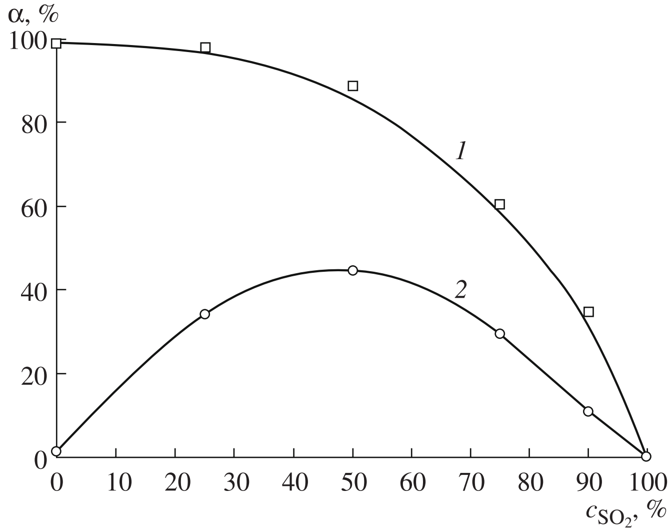

Fig. 3. Degree of bismuth chloride and iron chloride sublimation (percent of the starting) vs. Cl_2/ SO_2 in the vapor phase (contact time: 15 min at 600°C): (*1*) Bi and (*2*) Fe.

perature range. Analysis of the reaction products showed that iron chloride sublimation within 650–700°C obeys the equation

$$Fe_2O_3 + 3Cl_2 + 3SO_2 = 2FeCl_3 + 3SO_3. \qquad (5)$$

CONCLUSIONS

The above results show that several factors affect the rate of chemical sublimation of bismuth and iron chlorides. The degree of bismuth chloride sublimation from binary oxide mixtures in the presence of SO_2 increases noticeably only at relatively low temperatures (300–500°C), at which the mutual influence of the solid components is the strongest. The increase in the rate of the chemical reaction in the presence of Fe_2O_3 in this temperature range is due to the exchange reaction between $FeCl_3$ and $Bi_2(SO_4)_3$. Most iron transfers to sulfate. Iron chloride sublimation occurs only after bismuth is removed from the solid phase. Thus, selective $BiCl_3$ sublimation in the system in question is possible only within 300–500°C.

The role of the exchange reaction is reduced with temperature elevation, because $Bi_2(SO_4)_3$ degrades above 405°C. As a result, the effect of SO_2 on bismuth chloride sublimation is reduced. At the same time, the degree of $FeCl_3$ chemical sublimation increases; as a result, bismuth extraction selectivity decreases.

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