DISPROPORTIONATION OF THE BARIUM SULPHITE

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The rate of the disproportionation of the solid barium sulphite has been measured in an inert nitrogen atmosphere. The effect of the temperature, of the particle size of the solid, and of the presence of the water vapour in the gas phase were investigated. The value of the activation energy of the disproportionation of barium sulphite in dry nitrogen has been obtained as $E = 65.1$ kcal/mol. The particle size in the range from 0.10 mm up to 0.33 mm has practically no influence on the reaction rate. The presence of water vapour in the gas phase affects significantly the reaction rate of the disproportionation. It has been found that at constant degree of conversion of the barium sulphite ($x = 0.30$) the reaction rate is directly proportional to the partial pressure of water vapour in the range from 0 up to 20 Torr at the temperature of 678°C.

In connection with a study of kinetics of the reduction of the barium sulphite with hydrogen, an effect has been revealed of the partial pressure of water vapour which is one of the reaction products on the course of the thermal decomposition of the barium sulphite. The effect of the presence of water vapour on the disproportionation of barium sulphite has not yet been described. All existing studies of different authors[1-5] have been carried out in the atmosphere of a dry inert gas — most frequently nitrogen. Therefore, it has been necessary to study the disproportionation and the effect of variables on its course separately from the reduction of the barium sulphite with hydrogen which will be published in the next paper.

At elevated temperatures (above 600°C) and in the absence of oxygen, the barium sulphite decomposes into the barium sulphide and barium sulphate according to the equation

$$4\,BaSO_3 \;=\; BaS + 3\,BaSO_4 \qquad\qquad (A)$$
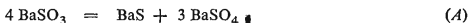
The first notion of the formation of the barium sulphide on heating the barium sulphite in the absence of air originates from Rammelsberg[1] already in the middle of the last century; the author mentioned above obtained a yellow remainder containing the barium sulphide on heating the

barium sulphite into red glow. Manchec[2] found that the decomposition according to the equation (A) is complete at a temperature of 900°C. The mechanism of the disproportionation of sulphites of metals of alkaline earths was treated by Ketov and Nichkovskij[3] which have studied the mentioned reaction at temperatures from 600°C up to 800°C in a nitrogen atmosphere. The decomposition of the sulphites of Ag, Tl[1], Ba, and Pb in a nitrogen stream at temperatures from 400°C up to 800°C has been investigated by Cola and Bissi[4] which report the disproportionation as a main reaction which takes place at heating the barium sulphite, whereas the dissociation takes place to a slight measure only (0·6—0·8% by weight of the barium sulphite). The kinetics of the disproportionation of the barium sulphite prepared by saturation of the suspension of barium carbonate with sulphur dioxide with gaseous sulphur dioxide has been measured by Shushunov, Sadovnikova, and Andrejev[5]. The measurements have been carried out in an atmosphere of dry nitrogen in a quartz tube at temperatures of 530—800°C. The reaction rate has been ascertained by gravimetric determination of the formed barium sulphate only, the amount of which expressed the degree of the disproportionation reaction. The same authors[5] have computed from the kinetic data the activation energy of the disproportionation reaction as $E = 23·6$ kcal/mole.

EXPERIMENTAL

Chemicals

The barium sulphite has been prepared by a heterogeneous reaction between the solution of the sodium sulphite and the solid barium carbonate at 25°C for 24 hours. The molar ratio of the sulphite to the carbonate in the solution amounted to 1·5 : 1. After the reaction has been finished, the product has been separated from the mother liquor, cautiously washed with water on a sintered glass filter and sucked off. The barium sulphite has been dried in air at the room temperature. The sample contained 88·9% by weight of the barium sulphite, 10% by weight of the barium carbonate, and 1—2% by weight of humidity.

The sodium sulphite has been a pure reagent of the firm Spolana (Neratovice) containing at least 97% by weight of the sodium sulphite.

The barium carbonate used for the conversion of the barium sulphite has been prepared by saturating the solution of barium hydroxide (analytical grade reagent of the firm Lachema, Brno) with the carbon dioxide from a pressure tank at 25°C. After washing and sucking off, the barium carbonate has been dried in air at room temperature.

The nitrogen contained 10^2 (sometimes even 10^3) p.p.m. of oxygen by order. The quality of the nitrogen was periodically checked with an oxygen analyser according to Hersch[6] adapted for measurement of low oxygen concentrations. In all the measurements carried out in an inert nitrogen atmosphere the carrier gas has been freed of oxygen in a "copper column"[7] which has been filled with a copper catalyst containing 42% by weight of the cupric oxide supported on silica. Before the use the catalyst has been activated with a nitrogen–hydrogen mixture at a temperature of about 220°C for several hours. If necessary, the nitrogen has been saturated with water vapour in a fritted glass saturator filled up with distilled water. The saturator has been thermostated at a temperature which corresponded to the required tension of water vapour in the carrier gas.

The metals used for calibration of the thermocouple were of the following quality. The antimony has been a twice sublimated product of the firm Kovohutě, Vestec. The aluminium has been zone melted (Kovohutě, Vestec). The zinc has been a granulated metal for laboratory purposes (import from the USSR). The remaining chemical used have been of analytical grade.

Apparatus

The kinetics of the disproportionation of the barium sulphite has been measured in a quartz reactor in which a platinum bed has been placed containing the solid. The platinum bed has been of cylindrical shape and has been closed at the lower end with a platinum net and at the upper end the cylinder has been conically widened. A precisely identical widening was in a quartz casing which served as a carrier of the platinum bed. The quartz casing has been ended at its lower part with a ground joint which fitted to another ground joint fused into the reactor. The platinum bed containing the layer of the barium sulphite could be removed from the reactor with the quartz casing. The design of the reactor was essentially identical with that used in the measurement of the gas–solid kinetics[8]. The reactor has been placed in an electrical resistance furnace. The temperature inside the furnace at the level of the bed has been measured by means of a Ni–NiCr thermocouple calibrated to melting points of zinc, aluminium, and antimony.

The nitrogen which served as an inert atmosphere in the measurement of kinetics of the heat decomposition has been taken from the pressure tank and subsequently led through a manostat, a capillary flow meter, a copper column for oxygen removal, drying columns filled with the molecular sieves (Calsit 5A) and the anhydrone into the reactor. In measurements in a humid nitrogen, a water saturator has been inserted behind the drying column thermostated with water from a constant temperature bath. Behind the saturator a demister has been inserted kept at the same temperature as the saturator. The partial pressure of the water vapour has been calculated from the feed rate, from the weight of the water vapour removed in a U-tube inserted behind the reactor and filled with anhydrone, and from the total atmospheric pressure which has been measured by means of a barometer Paulin (Stockholm).

The barium sulphite weighed (about 200 mg) in the platinum bed which has been tightly inserted into the quartz casing was placed in a quartz reactor. Before the heating had started, the reactor has been rinsed out with the nitrogen for an hour. After this period, the heating of the resistance furnace has been switched on, and the reactor was heated to the reaction temperature with the steady stream of nitrogen flowing through the bed. In the heating period the input of the furnace was constant and amounted to about 1000 W. The rate of furnace heating amounted to 12°C per minute. The adjusting of the required reaction temperature and its maintaining has been carried out by means of a compensation regulator KRp. After the reactor had reached the required temperature, the furnace input has been lowered to 450—500 W. From the moment when the compensation regulator has reached the adjusted temperature a precise temperature adjusting has been carried out by means of a variable furnace input during 10 minutes. After 10 minutes (the stabilization period) the measurement proper started either in a dry nitrogen or at various partial pressures of water vapour. The heating of the sample in the reactor up to the beginning of measurement has been carried out invariantly under a steady stream of dry nitrogen flowing through the bed at a feed rate of 100 ml per minute. The same flowing rate of the dry (or humid) nitrogen has been maintained during the measurement proper, too. The temperature in the furnace has been measured by means of a Ni—NiCr thermocouple in connection with a laboratory compensator QLK and a galvanometer Multiflex with an accuracy of 0.2°C, and during the measurement it varied in the range of ± 1°C round the mean value. The experiment has been ended in the way that the nitrogen stream has been interrupted and the reactor has been rapidly taken off from the furnace (maximally during 10 s.). After cooling to the laboratory temperature, the closed reactor has been rinsed out with the dry nitrogen, the platinum bed with the sample and with the quartz casing has been taken off from the reactor and weighed. The sample after the reaction was mostly sintered and formed an almost compact cylinder. A complete analysis of the reacted barium sulphite followed, consisting of the determination of the sulphide, sulphite and sulphate.

Analytical Methods

The analytical procedure which has been used for analogous systems by Förster and Kubel[9] has not yielded satisfactory results. The determination of sulphide makes difficulties probably because of the fact that the reacted barium sulphite forms an intimate mixture of the barium sulphite, sulphide and sulphate from which the barium sulphide cannot be quantitatively separated by means of common operations (such as dissolving, extracting, or simple displacing by means of the gaseous carbon dioxide). The following procedure proved to be the most suitable analytical method which determined the barium sulphide, sulphite and sulphate in the sample after reaction. The reacted sample has been finely rubbed in a small mortar and quantitatively transferred into a displacement flask. The boiled distilled water saturated with nitrogen has been used for transferring the sample into the flask and for rinsing out the mortar. The first portion of the sulphide has been displaced in the form of hydrogen sulphide (it amounted to 80—90% from the total amount of sulphide) from the aqueous suspension by means of carbon dioxide and the formed hydrogen sulphide has been absorbed in a solution of cadmium acetate. The displacement of the first portion of the hydrogen sulphide has been taking place initially at the laboratory temperature and subsequently at a gentle boiling for the same period. After this operation has been finished, the flask has been rinsed out with nitrogen and after rinsing, a diluted hydrochlorid acid (1 : 3) has been added. The remaining hydrogen sulphide and sulphur dioxide has been displaced with a stream of nitrogen under steady gentle boiling into a suspension of the small amount of cadmium hydroxide in a 0·4N-solution of potassium hydroxide. In this absorption solution, the hydrogen sulphide has been absorbed as cadmium sulphide and the sulphur dioxide remained in the solution in the form of potassium sulphite. The second portion of the cadmium sulphide has been separated from the sulphite solution by filtration under reduced pressure and added to the first portion of the sulphide. Both portions of the sulphide have been determined together iodometrically[10]. The sulphite contained in the filtrate has been determined also iodometrically after cooling. No significant deviations (0·1—0·2%) have been found in checking the method which has been carried out by determining the original unreacted barium sulphite in the way mentioned above (by displacing into the suspension of the cadmium hydroxide in the potassium hydroxide) and in comparing the results with those yielded by common iodometric determination of sulphites with the solid sample[10].

After separation of the sulphur dioxide and hydrogen sulphide, the remainder in the flask has been transferred quantitatively onto a filter (narrow pores) on addition of 25 ml of ethylalcohol, washed, and after drying burned and ignited. It has been weighed as barium sulphate. The balance of sulphur based on the original barium sulphite has been determined in most experiments with an accuracy better than ±2%.

RESULTS AND DISCUSSION

A total number of 80 experiments of disproportionation of barium sulphite has been carried out and the attention has been focussed on the effect of the particle size of the barium sulphite, on the effect of temperature, and on the effect of partial pressure of water vapour. The effect of particle size has been measured at a temperature of 678°C in a dry nitrogen and at two values of the partial pressure of water vapour (4·0 and 20·0 Torr) with two different sizes of particles (0·25—0·33 mm and 0·10 to 0·12 mm). The results of these measurements are illustrated in the Fig. 1. From the figure it is evident that the effect of particle size on the reaction course is practically negligible.

The effect of temperature has been investigated at three temperatures in the dry nitrogen and at two temperatures at a partial pressure of water vapour of 4·0 Torr (Fig. 2). The reaction course in the dry nitrogen in a temperature range of 639 to 678°C is not significantly affected by a temperature change of 39°C. The susceptibility is increased in the presence of water vapour as it is evident from a comparison of the curves *1*, *2*, and *3*. A study of the given reaction at equidistant temperatures round 718°C has not proved to be feasible because of the fact that at the beginning of measurement more than 50% of the original barium sulphite has been decomposed during the heating to the temperature required and during the subsequent temperature stabilization. It is evident from the Fig. 2 that the effect of temperature begins to be important at temperatures above 678°C, whereas below this temperature the effect of temperature is not significant.

The most important effect has been found in the presence of water vapour in the carrier gas. At a temperature of 678°C the measurements have been carried out in dry nitrogen and at three values of the partial pressure of water vapour (Fig. 3). It is evident from the comparison of the curves *1—4* that the reaction in the dry nitrogen takes place rather slowly at a temperature of 678°C and that it is significantly accelerated by the presence of water vapour. The positive effect is especially outstanding at higher tensions of the water vapour (10·0 and 20·0 Torr). At a temperature of 639°C, the effect of water vapour content is very small (Fig. 2, curve *1*);
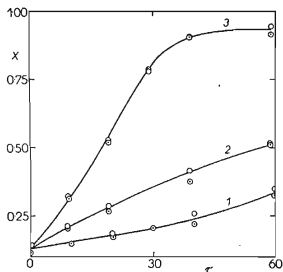

Fig. 1

Effect of Particle Size and of Water Vapour Content in Gas Phase on Disproportionation of Barium Sulphite at Temperature of 678°C

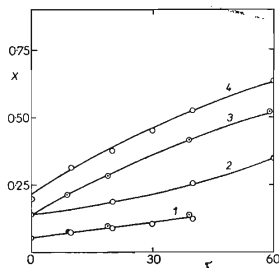○ 0·25—0·33 mm, ⊙ 0·10—0·12 mm; *1* dry nitrogen, *2* $p_{H_2O} = 4·0$; *3* $p_{H_2O} = 20·0$.

Fig. 2

Effect of Temperature and of Water Vapour Content in Gas Phase on Disproportionation of Barium Sulphite

○ Dry nitrogen, ⊙ $p_{H_2O} = 4·0$; *1* 639°C; *2, 3* 678°C; *4* 694°C.

this finding has been verified in two experiments with a higher tension of water vapour (20·0 Torr) at this temperature.

A typical course of the disproportionation of the barium sulphite at a temperature of 678°C in dry nitrogen and at a partial pressure of water vapour of 20·0 Torr is illustrated in the Fig. 4. In this figure the individual curves represent the decrease of the sulphite content (curves *3, 4*), the increase of the sulphate content (curves *5, 6*), and of the barium sulphide (curves *1, 2*) in mol percents in dependence on time. None of the curves in the Fig. 1—4 does start from the origin of coordinates since the barium sulphite is already partially decomposed during the heating to the reaction temperature. The degree of conversion at the start of measurement, x_0, depends on the temperature at which the measurement has been carried out (at a temperature of 678°C it amounted to $x_0 = 0·13—0·14$, and at 639°C $x_0 = 0·05$) and to a small extent on the particle size (at a temperature of 678°C and for the particle size of 0·25 to 0·33 mm $x_0 = 0·13—0·14$ and for 0·10—0·12 $x_0 = 0·11—0·12$). The last named effect, however, may be ascribed rather to the errors in reproducibility of determinations of the reaction start than to a real effect of particle sizes which has been verified in experiments with the partical sizes of 0·17—0·20 mm.

From the reaction courses measured, the value of the activation energy of disproportionation in dry nitrogen has been computed. The following procedure has
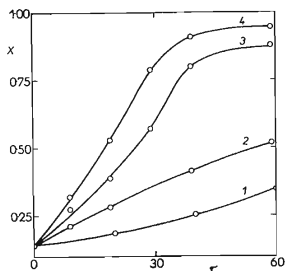

FIG. 3

Effect of Water Vapour Content in Gas Phase on Disproportionation of Barium Sulphite at Temperature of 678°C

1 Dry nitrogen; *2* $p_{H_2O} = 4·0$; *3* $p_{H_2O} = 10·0$; *4* $p_{H_2O} = 20·0$.
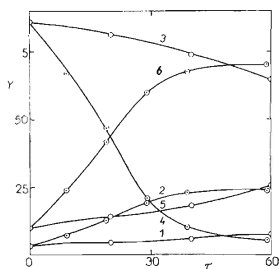
FIG. 4

Typical Course of Changes of Individual Component Content in Disproportionation of Barium Sulphite at Temperature of 678°C in Dry and Humid Nitrogen in Mol Percents Y

○ Dry nitrogen; ⊙ $p_{H_2O} = 20·0$; *1, 2* BaS; *3, 4* BaSO$_3$; *5, 6* BaSO$_4$.

been used. If the reaction rate r may be expressed as a function of temperature and of the degree of conversion in the form

$$r = k_{(T)}f_{(x)} \qquad (1)$$

a relation is obtained on differentiating according to the temperature at a constant degree of conversion

$$\mathrm{d}\ln r/\mathrm{d}T = \mathrm{d}\ln k_{(T)}/\mathrm{d}T. \qquad (2)$$

By comparison of the equation (2) with the Arrhenius equation at constant degree of conversion, x, we obtain

$$\mathrm{d}\ln k/\mathrm{d}T = \mathrm{d}\ln r/\mathrm{d}T = E/RT^2 \qquad (3)$$

and on integrating the equation (3) within the limits of r_1, r_2, and T_1, T_2 at constant x, an expression is obtained

$$\ln(r_2/r_1) = (-E/R)(1/T_2 - 1/T_1). \qquad (4)$$

If the reaction rate r is defined as
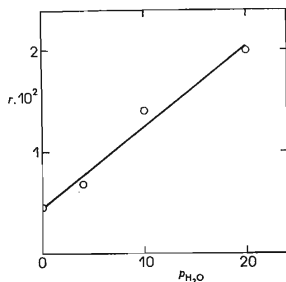
$$r = \mathrm{d}x/\mathrm{d}\tau, \qquad (5)$$

Fig. 5

Dependence of Reaction Rate of Disproportionation of Barium Sulphite at Constant Degree of Conversion of $x = 0.30$ on Partial Pressure of Water Vapour at 678°C

then the tangent slope of the curve x *vs.* τ for a given degree of conversion x gives the value of the reaction rate, and the activation energy may be computed by means of the equation (4) from the ratio of tangent slopes at the same degree of conversion, x, at two temperatures, T_1 and T_2. The tangents were evaluated graphically for the degree of conversion of $x = 0.30$ at temperatures of 678°C and 694°C, and the value of the activation energy of disproportionation of the barium sulphite in dry nitrogen has been computed as $E = 65.1$ kcal/mol. This value of activation energy for heat decomposition in dry nitrogen differs by almost threefold from the value given by the authors mentioned previously[5]. This difference may be explained by the fact that the reactivity of solids is influenced predominantly by the method of preparation of the solid phase, and the barium sulphite used in this work has been prepared in another way than the barium sulphite of the authors[5].

The tangents slopes of reaction courses for four values of partial pressure of the water vapour at a temperature of 678°C have been evaluated graphically for the same degree of conversion of $x = 0.30$. The values of the reaction rates at constant degree of conversion in dependence on the partial pressure of water vapour are given in the Fig. 5. from which it is evident that the rate of disproportionation at a constant degree of conversion $(x = 0.30)$ and at a temperature of 678°C is directly proportional to the partial pressure of water vapour in the range from 0 up to 20 Torr.

It is evident from the comparison of dependences of the reaction courses of the barium sulphite disproportionation on the partial pressure of the water vapour and on the temperature that the effect of the partial pressure of water vapour on the rate of disproportionation in the studied range is more important than the effect of temperature. This conclusion is of significance for the further study of kinetic properties of the barium sulphite. *E.g.* in the reduction of the barium sulphite with hydrogen the water vapour, which is a reaction product, can significantly influence the rate of the disproportionation reaction taking place in parallel.

LIST OF SYMBOLS

E	activation energy (kcal/mol)
k	rate constant of disproportionation
p_{H_2O}	partial pressure of water vapour in the gas phase (Torr)
r	reaction rate (min^{-1})
R	gas constant (cal/mol^{-1} °K^{-1})
τ	time (min)
T	absolute temperature (°K)
x	degree of conversion of barium sulphite
Y	mol percent of reacting component (sulphite, sulphate, or sulphide)

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