FORMATION OF SODIUM DISULPHITE BY REACTION OF SOLID SODIUM SULPHITE WITH GASEOUS SULPHUR DIOXIDE

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The formation of sodium disulphite in a heterogeneous reaction between solid sodium sulphite and gaseous sulphur dioxide has been investigated in a fixed-bed reactor at temperatures from 40 up to 80°C in the presence of water vapour. The partial pressure of the sulphur dioxide was in the range of 1·2 to 7·5 kPa and that of the water vapour amounted to 1·0—6·5 kPa. The study has been aimed at finding optimum conditions for the formation of the disulphite according to the final degree of conversion. It has been found that the final degree of conversion depends primarily on the content of water vapour in the gas phase and on the temperature, the reactivity of the sodium sulphite being significantly affected by the way of its preparation.

The usual procedure for preparing the sodium disulphite consists in the saturation of a sodium carbonate solution with gaseous sulphur dioxide, the intermediate product being sodium hydrogen sulphite. The aim of the present paper consisted in investigating the conditions of the formation of sodium disulphite by a heterogeneous reaction between gaseous sulphur dioxide and the solid sodium sulphite.

The production of sodium disulphite by a dry process is mentioned in a German patent application[1]. Its authors state, that it is possible to prepare sodium disulphite of the grade from 96 to 98% in a continuous process at temperatures from 40 to 50°C, using a roasting gas containing 6·5 – 7% of the sulphur dioxide and in the presence of water vapour (of about 3%). The necessary humidity is supplied by means of the humid gas, of the initial sodium carbonate, or the water is injected into the reaction space. A not too high intensity of this process is evident from the mean residence time of the solid in the reactor amounting to tens of hours and from the mean residence time of the gas which amounted to tens of seconds. Preparation of sodium disulphite by a reaction of sulphur dioxide with solid sodium carbonate has been investigated in full detail in the paper of Blyakher and Laryushkina[2]. The authors investigated the course of consecutive reactions in a fluid bed reactor at temperatures from 40 to 70°C with a content of the sulphur dioxide in the air stream from 1 to 11%, of the humidity of soda 1 – 22%, and of the gas humidity from 1·7 to 17% It has been found, that under given conditions, it is possible to obtain a product of the grade of 89%.

Recently, the existence of an active form of the sodium carbonate has been discovered[3-5] which is distinguished by an extremely high reactivity with respect to sulphur dioxide, and by a high degree of conversion to sulphite attaining nearly the stoichiometric conversion. In addition it has been found, that the sodium sulphite prepared from the active sodium carbonate by reaction *in situ* exhibits an increased reactivity even in oxidation when compared with the sodium sulphite prepared by a wet process[6,7]. Therefore, it was possible to assume, that the sodium sulphite prepared in the former way will exhibit an increased reactivity even towards sulphur dioxide – similarly as its parent substance does – so that it would be possible to prepare the sodium disulphite by means of the following couple of equations:

$$\mathrm{Na_2CO_3}(s) + \mathrm{SO_2}(g) = \mathrm{Na_2SO_3}(s) + \mathrm{CO_2}(g) \qquad (A)$$

$$\mathrm{Na_2SO_3}(s) + \mathrm{SO_2}(g) = \mathrm{Na_2S_2O_5}(s)\,. \qquad (B)$$

EXPERIMENTAL

The measurements have been carried out on a flow apparatus described previously[8]. The isobaric and isothermal conditions have been maintained by means of a small pressure drop along the bed, of an efficient temperature control of the reactor, and of a sufficient gas velocity. The sodium sulphite used in the measurements has been prepared *in situ* by a heterogeneous reaction of the solid anhydrous sodium carbonate with gaseous sulphur dioxide — with exception of a set of experiments in which the effect of genesis of the parent substance was investigated. The anhydrous sodium carbonate has been prepared by thermal decomposition of the sodium hydrogen carbonate *in situ* in a stream of nitrogen. The precipitated sodium hydrogen carbonate has been prepared by a procedure described previously[3]. In experiments concerning the effects of genesis of the parent substance, the sodium sulphite (A.G. Merck) has been used. The sulphur dioxide and the lamp nitrogen have been taken from pressure tanks. The remaining reagents were of A.G. purity.

Thirty kinetic measurements have been evaluated, which have been carried out in a temperature range from 40—80°C with the nitrogen as a carrier gas at partial pressures of the sulphur dioxide from 1·2 up to 7·5 kPa and at water vapour partial pressures from 1·0 up to 6·5 kPa. The content of the sulphur dioxide in the gas phase was determined by conductance as sulphuric acid after absorption in a hydrogen peroxide solution, as described previously[3]. The final degree conversion of the solid was determined by a standard iodometric method.

RESULTS AND DISCUSSION

Since the investigated formation of the sodium disulphite is represented by the second reaction from the couple of consecutive reactions (A) and (B) taking place in the solid layer, it was necessary to express the degree of conversion of the solid phase in the whole extent of both reactions. The degree of conversion, x, used in this paper, signifies the ratio of the amount of the sulphur dioxide in the solid phase found analytically to the corresponding amount on the solid phase which is equal to the amount of the initial sodium carbonate.

The effect of humidity of the gas phase on the final degree of conversion is demonstrated in Fig. 1. In the range of partial pressures of the water vapour up to 1 kPa, the

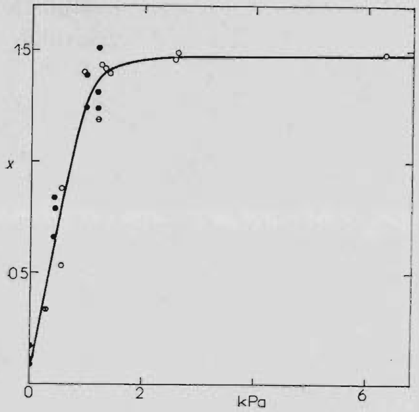

FIG. 1

Experimental dependence of final degree of conversion on partial pressure of water vapour. $t = 54°C$; $\tau \sim 30$ min; ⊖ $p_{SO_2} = 1{\cdot}2$ kPa; ● $p_{SO_2} \approx 3$ kPa; ○ $p_{SO_2} \approx 7$ kPa

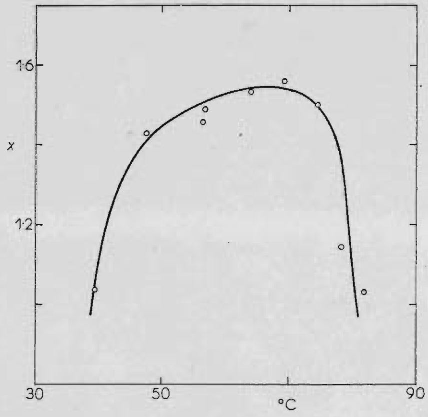

FIG. 2

Experimental dependence of final degree of conversion on temperature. $p_{H_2O} = 2{\cdot}53$ kPa; $p_{SO_2} \sim 4{\cdot}7$—$7{\cdot}6$ kPa; $\tau \sim 40$ min

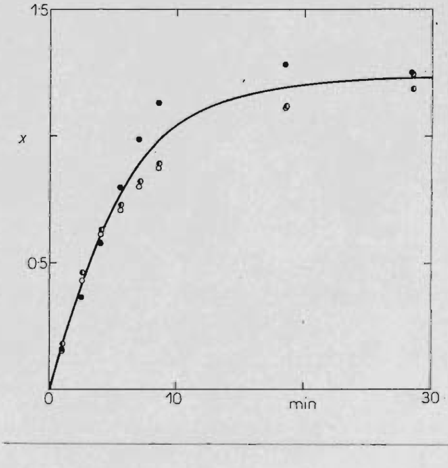

FIG. 3

Experimental dependence of degree of conversion on reaction time. ○ ● ◐ $p_{H_2O} = 1{\cdot}16$ kPa; $p_{SO_2} \sim 1{\cdot}2$—$3{\cdot}5$ kPa; $t = 54°C$

final degree of the solid conversion increases approximately linearly with the content of water vapour in the gas phase. At partial pressures of the water vapour above 2 kPa, the content of the water vapour is of no effect on the final degree of conversion. Likewise it is evident from Fig. 1, that the partial pressure of sulphur dioxide in the range above 1·3 kPa has no significant effect on the final degree of conversion of the solid to disulphite.

The temperature dependence of the final degree of the solid conversion exhibits a maximum in the interval from 50 to 75°C (Fig. 2).

The prolongation of the reaction time above 20 minutes does not result under typical reaction conditions ($p_{SO_2} > 1{\cdot}3$ kPa, $p_{H_2O} > 1{\cdot}3$ kPa) in an increase of the degree of conversion of the solid phase to disulphite. A typical time dependence of the degree of conversion is shown in Fig. 3.

The reactivity of the sodium sulphite depends significantly on the way of its preparation. Two samples of the sodium sulphite were compared. The sample of Merck (analytical chemical) was quite unreactive under conditions, where the highest degree of conversion has been attained with samples prepared by the heterogeneous reaction *in situ*. Possible explanation of the different reactivity of both samples may be seen in surface effects. If the reaction with conversion of about 60% would be assumed to take place only on the surface of the particles a diameter of the order of 10^{-10} m (in the spherical approximation) would have to be assigned to them.

Under approximate optimum reaction conditions ($p_{H_2O} = 6{\cdot}4$ kPa, $p_{SO_2} = 7{\cdot}2$ kPa, $t = 80$°C, $\tau = 40$ min.), a degree of conversion of the solid phase to sodium disulphite of 1·62 has been attained in the couple of consecutive reactions (*A*) and (*B*), which corresponds to 71·1 weight percent of the disulphite in the solid phase in a mixture with the sulphite. This value is in a rather good agreement with results of the authors[2], who obtained the final degree of conversion to disulphite within the limits from 1·54 up to 1·75 under similar conditions in a fluidized bed, however, with a sodium carbonate which has been under optimum conditions humidified in advance to a content of 6·7–15 wt.% of water. The fact that according to reaction (*B*) no higher degree of conversion to the disulphite than $x = 1{\cdot}6$ has been attained, as compared with an almost total conversion of the active carbonate (reaction (*A*)), can be explained on the basis of a different nature of both reactions. Whereas the substitution reaction (*A*) is accompanied by only a small change of the molar volume (11·4%), the subsequent addition reaction (*B*) is connected with its significant increase (269%). Therefore, the solid phase ($Na_2S_2O_5$) formed probably hinders the access of the sulphur dioxide to the phase boundary, where the reaction takes place, and in this way the attainable degree of conversion of the solid decreases.

The dependence of the degree of conversion of the solid on the partial pressure of water vapour shows a significant saturation character, which is in agreement with the role of adsorption in the same way as it was respected in the proposal of the mechanism of formation of the sodium sulphite[9]. The observed independence of the degree of conversion of the solid phase on the partial pressure of the sulphur dioxide may be also interpreted by adsorption of the sulphur dioxide, which is practically independent of pressure in the region of its higher values[9]. The decrease of the degree of conversion with temperature may be interpreted in two ways: either by the effect of chemical equilibrium in the reaction (B) or by a decrease of the adsorption equilibrium constant of water vapour, eventually by a combination of both.

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