FORMATION OF SODIUM DISULFITE IN A SOLID–GAS SYSTEM

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Received March 2, 1990
Accepted December 28, 1990

The formation of sodium disulfite by the heterogeneous reaction of solid active sodium sulfite with gaseous sulfur dioxide in the presence of water vapour was investigated over the temperature range of 293 to 393 K at SO_2, H_2O and O_2 partial pressures of 1·2—7·4, 1·2—6·4 and 0—11·3 kPa, respectively. The effect of the reaction time was also examined. Kinetic measurements were supplemented with the determination of the equilibrium dissociation pressure of SO_2 in contact with sodium sulfite at 373·15 K. The major aim of the work was to establish the optimum conditions for attaining the maximum degree of conversion of the solid reactant to sodium disulfite. The conditions for the formation of virtually pure sodium disulfite were found.

Methods for the preparation of disulfites are usually divided into two groups, viz. "wet" methods, performed from solutions or suspensions, and "dry" methods, consisting in action of sulfur containing gases on solid substances. The former methods are predominantly used in the industry although they are rather highly energy-demanding.

Sodium carbonate or sodium hydrogen carbonate are used as the starting substances in the dry methods[1]. In the former case, the process follows the pathway:

$$Na_2CO_3 + SO_2 = Na_2CO_3 + CO_2 \qquad (A)$$

$$Na_2SO_3 + SO_2 = Na_2S_2O_5 \qquad (B)$$

and takes place only in the presence of some amount of water, whereas absolutely dry substances do not react[1–4].

The side oxidation giving sodium sulfate,

$$Na_2SO_3 + \tfrac{1}{2}\,O_2 = Na_2SO_4 \qquad (C)$$

is eliminated in some procedures by the use of antioxidants[1,2,5,6]. Compared with wet procedures of sodium disulfite preparation, the dry ones allow a number of technological operations to be eliminated, some of them energy demanding. Drawbacks of existing dry procedures, on the other hand, include a low intensity of the process and relatively low conversion of the solid to sodium disulfite.

In the study of the formation of sodium disulfite by heterogeneous reaction of solid sodium sulfite with gaseous sulfur dioxide at 313–353 K, the genesis of the solid reactant was found to be the most important factor with respect to the reaction course. The active form of anhydrous sodium sulfite is formed by the reaction of solid active sodium carbonate with sulfur dioxide, whereas the inactive one is obtained by preparation from solution. During a kinetic study[3] of reaction (*B*), however, conditions were found for the formation of a product containing 81% sodium disulfite only.

In the present work, the kinetics of reaction (*B*) was investigated over the temperature region of 293 to 393 K with a view to establishing conditions for the formation of high-percentage sodium disulfide in the solid phase–gas system. In addition, the equilibrium dissociation pressure of sulfur dioxide in contact with sodium disulfite at 373·15 K was determined.

EXPERIMENTAL

Kinetic measurements were carried out on a flow apparatus[7] in a fixed-bed reactor at atmospheric pressure. The gas contact time was of the order of hundreths of a second. Isobaric and isothermal conditions were secured by means of a small pressure drop along the bed, of an efficient thermostatting of the reactor, and of a sufficient gas flow rate.

The final degree of conversion of the solid was determined iodometrically after termination of the experiment. If the titrimetric analysis indicated that the solid product was pure sodium disulfite, the composition of the solid was also examined by X-ray powder diffractometry. The sulfur dioxide content of the gas mixture was determined conductometrically as sulfuric acid, after absorption in hydrogen peroxide solution.

Chemicals. Sodium sulfite was prepared in situ by the heterogeneous reaction (*A*). Anhydrous sodium carbonate was obtained by thermal decomposition of sodium hydrogen carbonate in situ in a stream of nitrogen. Precipitated $NaHCO_3$ was prepared as described previously[8]. Nitrogen (carrier gas) was of the grade used in the production of filament lamps. The other chemicals used were of reagent grade purity.

Equilibrium measurement. The dissociation pressure of sulfur dioxide in contact with sodium disulfite was measured at a constant volume after evacuating the measuring part of the apparatus and thermostatting the vessel containing the sample. The pressure of sulfur dioxide was measured with a differential mercury pressure gauge. The mercury level difference was read with a cathetometer with a precision of 0·005 mm. In view of the low rate of the decomposition reaction, the pressure and temperature gradients in the solid sample layer and between the reaction space and the pressure gauge or thermometer could be neglected. The volume of the measuring part of the apparatus was about 120 ml.

RESULTS AND DISCUSSION

Kinetic Study of Reaction (B)

The primary data were the values of the final degree of conversion of the solid to sodium disulfite in dependence on the gas composition, temperature, and reaction time. As in our previous papers, the degree of conversion is the ratio of the analytically established number of moles of sulfur dioxide to the total number of moles of the solid phase. It can attain values of 0 to 2, values within the 1 – 2 range corresponding to the formation of $Na_2S_2O_5$.

The effect of partial pressures of sulfur dioxide $p(SO_2)$, that of water vapour $p(H_2O)$, and the effect of temperature T on the final degree of conversion of the solid x are shown in Fig. 1. The fact that the final degree of conversion of the solid is independent of the partial pressure of sulfur dioxide at temperatures up to about 328 K can be explained in terms of the assumption that the conversion is controlled by the interfacial chemical reaction (B) and that in the pressure range applied the adsorption of sulfur dioxide on the interface is virtually pressure-independent. The decrease in the final degree of conversion to approximately $x = 1$, corresponding to the conversion of the solid to pure Na_2SO_3, which for $p(SO_2) = 1{\cdot}7$ kPa occurs at about 333 K and for $p(SO_2) = 4{\cdot}0$ kPa at about 363 K, can be explained by the chemical equilibrium establishing in reaction (B). This interpretation is consistent with the observed equilibrium dissociation pressure of SO_2 in contact with $Na_2S_2O_5$ at 373·15 K.

The fact that the final degree of conversion is unaffected by increasing the water vapour partial pressure above 3·0 kPa at temperatures lower than 328 K and above 1·4 kPa at higher temperatures can also be explained taking into account the role of adsorption in the process. The steep increase in the final degree of conversion of the solid with decreasing temperature over the 313 – 293 K range at $p(H_2O) =$

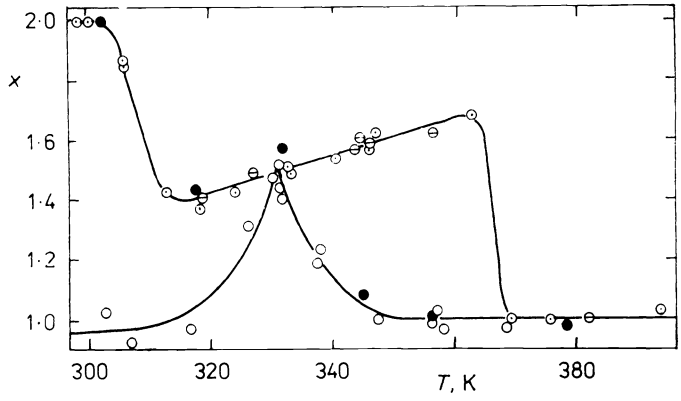

FIG. 1

Dependence of the final degree of conversion of the solid on temperature and gas phase composition; $p(SO_2)$, $p(H_2O)$ in kPa: ○ 1·7; 1·4; ● 1·7, 3·0; ⊙ 4·0, 3·0; ⊖ 4·0, 6·0

= 3·0 kPa is probably related with the fact that over this temperature range the water vapour partial pressure approaches its equilibrium value in contact with pure water. Although the mechanism comprising capillary condensation in pores of the reacting solid can also be considered, it is not very likely because no significant quantities of micropores have been found in measurements on samples of active sodium carbonate and sodium sulfite[9].

TABLE I

Effect of reaction conditions on the final degree of conversion x of the solid to sodium disulfite

Partial pressure, kPa			T K	τ min	W^a	x
SO_2	H_2O	O_2				
1·7	3·1	0	296·75	8	1·3	1·76
1·9	2·8	0	296·55	15	2·2	1·88
1·7	2·9	0	296·35	30	5·8	1·88
1·6	3·2	0	296·15	60	9·1	2·00
4·0	3·0	0	296·25	15	6·4	1·96
4·1	3·0	0	296·05	30	12·2	2·00
4·2	3·1	0	296·35	60	36·2	2·00
1·6	3·0	11·3	297·15	8	1·7	1·62
1·7	3·2	11·3	296·85	15	3·3	1·62
1·6	3·0	11·2	296·85	30	5·6	1·94
1·8	2·9	11·4	297·05	60	10·4	1·96
1·9	2·8	11·1	297·25	120	24·5	1·94

[a] Dimensionless degree of stoichiometric load of the bed.

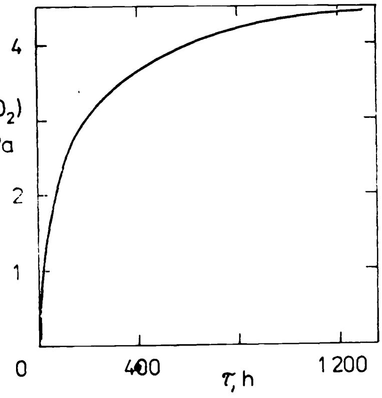

FIG. 2

Observed time dependence of the dissociation pressure of SO_2 in contact with solid $Na_2S_2O_5$ at 373·15 K

The effect of the reaction time τ and oxygen content of the gas mixture $p(O_2)$ on the final degree of conversion of the solid x was investigated in conditions where the remaining variables were approximately optimum with respect to the final degree of conversion. The results are summarized in Table I. The time necessary for the complete transformation of the solid to sodium disulfite does not exceed 60 min at $p(SO_2) = 1{\cdot}7$ kPa and 30 min at $p(SO_2) = 4{\cdot}1$ kPa, which corresponds, under the condition sused, to the introduction of approximately ninefold and twelvefold stoichiometric amounts of SO_2, respectively. In the presence of oxygen at $p(O_2) = 11{\cdot}3$ kPa, the final degree of conversion did not decrease more than by 2% at 297 K. (It is noteworthy that at 578 K, Na_2SO_3 prepared by the heterogeneous reaction (*A*) was observed[10] to be oxidized intensively by oxygen in air.)

It can be concluded that active sodium sulfite is converted completely to sodium disulfite at $p(SO_2) = 1{\cdot}7 - 6{\cdot}0$ kPa, $p(H_2O) = 3{\cdot}0$ kPa, $T = 293 - 299$ K and $\tau = 30 - 60$ min.

Dissociation Pressure of Sulfur Dioxide in Contact with Sodium Disulfite

The dissociation pressure was measured at 373·15 K. The results, in the form of the time dependence of the sulfur dioxide pressure, are shown in Fig. 2. The experiment was terminated after 1 300 h, when the pressure was virtually constant. Its value was 4·43 kPa. The degree of decomposition of the starting sulfur disulfite was approximately 0·7%. With regard to the procedure applied, the obtained dissociation pressure value must be regarded as the minimum one; it is, however, reasonable to assume that it is close to the actual equilibrium value. The value reported by Epifanov and Kunin[11] for the above temperature is mere 0·7466 kPa. The large difference between the two values is probably due to the conditions in the work[11] being far from equilibrium, which establishes very slowly.

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Translated by P. Adámek.