

A New Look on the Oxidation Process of Sodium Sulfit

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The article presents a new mechanism, suggested for the oxidation process of solid sodium sulfite. The process was found to proceed via four thermal decomposition steps. The first of them (257–318°C) is characterized by formation of sodium pentasulfate, $\text{Na}_2\text{O}\cdot 5\text{SO}_3$ (which was not detected before by any investigator) and sodium metal which oxidized to Na_2O and NaO_2 during the second step (318–640°C). The third step (645–790°C) is characterized by formation of sodium sulfate, sodium sulfide and sulfur dioxide. The first and second compounds are formed as a result of thermal dissociation of sodium sulfite at *ca.* 600°C, whereas the first and third ones are produced as a result of interaction of sodium sulfide and sulfur trioxide resulted from dissociation of sodium pentasulfate at *ca.* 700°C. The liberated sulfur oxides (SO_2 and SO_3) reacted with sodium oxides leading to the formation of Na_2SO_4 and Na_2SO_3 during the fourth step (> 790°C). The further fate of the newly formed species of sulfite is the same as described before, so that it was found experimentally that the percentages of the sulfite salt in the decrease gradually above 700°C and reaches about 0.1% at 1000°C.

INTRODUCTION

Sodium sulfite is known by its moderate reducing power among the reducing agents. This moderate power is considered as the key for its uses in various industrial, pharmaceutical and biological applications. It is used to bleach wool, silk¹, textiles² and paper³. It is employed as a preservative for fruits and vegetables⁴ and to prevent raw solutions from colouring upon evaporation⁵. It is, also, widely used as an initiator for preparation of numerous types of organic compounds and polymers⁶.

Due to the importance of the salt as a deoxidizer in numerous pharmaceutical preparations⁷, the chemical process of oxidation of the salt in different aqueous media was extensively studied by many authors^{8–12}. They found that the oxidation process depends on several factors such as concentration of the salt, oxygen pressure and both concentration and type of the added cations used as catalysts^{8–12}.

The oxidation process of the solid compound by oxygen at moderate or elevated temperature was the subject of the studies carried out by few authors^{13–15}. It was suggested by some of them that it is oxidized directly to

sodium sulfate through a very simple oxidation mechanism^{13, 14}, whereas a more complicated one was suggested by Foerster *et al.*¹⁵ He stated that the starting salt (Na_2SO_3) is always found together with some other reaction products, *e.g.*, Na_2SO_4 , Na_2S and SO_2 upon heating at different temperatures even at 1200°C .

The pronounced difference between the two reported postulations led us to devote the present study to investigate, extensively, such process at a range of temperatures between 250 and 1000°C using chemical and thermal analyses, and X-ray diffraction patterns. The results of the present study will be taken as a guide during the investigation and characterization of reaction products resulted from the interaction between the salt and ammonium metavanadate hoping to prepare a catalyst used for oxidation of SO_2 in the industry of sulfuric acid¹⁶.

EXPERIMENTAL

Chemicals: The anhydrous salt of sodium sulfite (minimum assay, iodometric, 96%), iodine and sodium thiosulfate were obtained from BDH Company, England.

Heating process of sodium sulfite: The salt (Na_2SO_3) was heated gradually ($10^\circ\text{C}/\text{min}$) from room temperature to the desired one and kept constant for 4 h at that temperature. The heating temperatures are 250, 300, 400, 500, 600, 700, 800, 850, 900 and 1000°C .

X-Ray diffraction patterns (XRD): The X-ray diffraction patterns of sodium sulfite before and after heating at different temperatures were obtained at room temperature using a Philips diffractometer (type PW 1051) employing Ni-filtered $\text{Co } \alpha\text{K}$ radiation ($\lambda = 1.7903 \text{ \AA}$). The X-ray tube was operated at 36 kV and 16 mA. The diffraction angle 2θ was scanned at a rate of $2\theta \text{ min}^{-1}$.

Thermal analysis: The thermogravimetric analysis of sodium sulfite was carried out using Perkin-Elmer Delta Series (TGA 7) thermoanalyzer. The rate of heating, in the static air, was $10^\circ\text{C min}^{-1}$.

Chemical analysis: The percentages of reducing compounds such as sodium sulfide and/or sodium sulfite, in the salt sample and different heating products, were determined according to the known iodometric method of analysis¹⁷.

RESULTS AND DISCUSSION

The thermal analysis of sodium sulfite was studied by using thermogravimetric analyser whereas the characterization of different thermal products was carried out by means of X-ray diffraction patterns and iodometric chemical analysis.

By inspection of the TG curve of sodium sulfite it can be seen that the thermal decomposition process of the salt consists of four successive and not separated steps (Fig. 1). The first one shows a gradual increase in weight loss of the sample starting from 257°C and reaches maximum at 318°C with a value equal to 2.47% at the last temperature. By inspection of the results of X-ray diffraction patterns presented in Fig. 2, it is suggested that this loss may be considered as a resultant of increase in weight due to oxidation of 39.30% of the liberated sodium and decrease in weight due to volatilization of 60.70% of the metal which usually

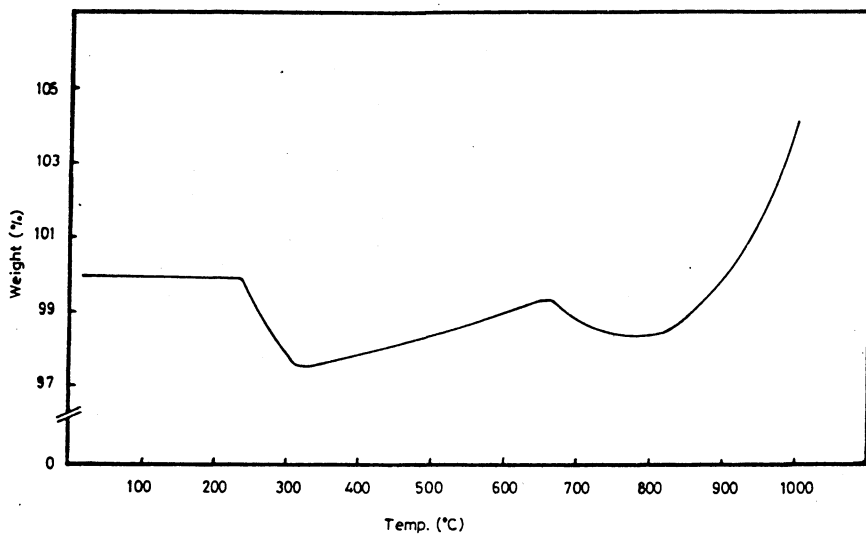


Fig. 1 TG trace of sodium sulfite in air (heating rate = 10°C)

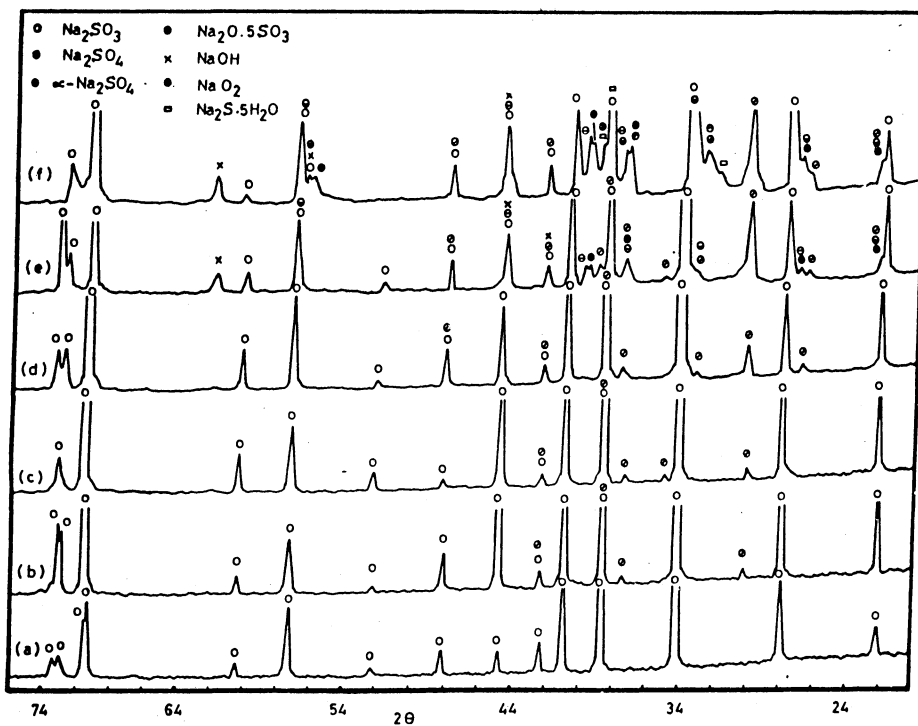
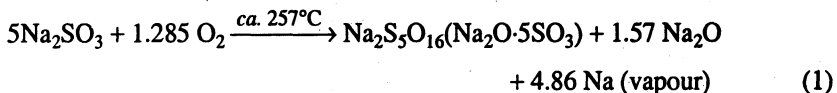


Fig. 2 X-ray diffraction patterns of sodium sulfite (a) and products resulted from heating of the salt at 250 (b), 300 (c), 400 (d), 500 (e) and 600°C (f) for 4 h, using $\text{Co K}\alpha$ irradiation and nickel filter.

melts at 97.70°C¹⁸. Based on this hypothesis the previous processes may be represented by the following equation:



The observed gradual increase in weight loss may be attributed to the gradual increase of the vapour pressure of liquid sodium by increasing the temperature of heating. The liberation of sodium metal was confirmed from the appearance of sodium hydroxide species which resulted from the reaction of the metal with water vapour after cooling of the heated sample, as appears from X-ray diffraction patterns (Fig. 2). The appearance of sodium oxides and/or sodium hydroxides at temperatures higher than 318°C as appears from X-ray diffraction patterns (Figs. 2 and 3) and results presented in Table-1 may be attributed to the difference in thickness between the heated sample in case of thermal analysis experiment and that heated in the muffle furnace.

TABLE-1
REACTION PRODUCTS OF THERMAL DECOMPOSITION OF Na₂SO₃ AT
DIFFERENT TEMPERATURES

Temp. (°C)	Product
25	Na ₂ SO ₃
250	Na ₂ SO ₃ , Na ₂ S ₅ O ₁₆ (traces)
300	Na ₂ SO ₃ , Na ₂ S ₅ O ₁₆ (traces)
400	Na ₂ SO ₃ , Na ₂ S ₅ O ₁₆
500	Na ₂ SO ₃ , Na ₂ S ₅ O ₁₆ , α-Na ₂ SO ₄ , Na ₂ SO ₄ , NaOH
600	Na ₂ SO ₃ , Na ₂ S ₅ O ₁₆ , Na ₂ SO ₄ , α-Na ₂ SO ₄ , NaO ₂ , NaOH, Na ₂ S·5H ₂ O*
700	Na ₂ SO ₃ (traces), Na ₂ S ₅ O ₁₆ , Na ₂ SO ₄ , α-Na ₂ SO ₄ , NaOH
800	Na ₂ S ₅ O ₁₆ , Na ₂ SO ₄
850	Na ₂ S ₅ O ₁₆ , Na ₂ SO ₄
900	Na ₂ S ₅ O ₁₆ , Na ₂ SO ₄
1000	Na ₂ SO ₄

*The appearance of water molecules in the formula may be due to adsorption of water vapours from the humid atmosphere during the cooling process.

It is worthy to mention that sodium pentasulfate salt was not detected in the previous studies concerned with the oxidation of sodium sulfite¹³⁻¹⁵, which may be due to the lack of ASTM card on the compound since it was firstly prepared by Vanderpe¹⁹ in 1967.

The second step, as can be seen from Fig. 1, is concerned with the heating temperature above 318°C where it was observed that the weight of the sample increases gradually and reaches maximum to about 100% of the weight of the sample at ca. 640°C. The last phenomenon may be attributed to the oxidation of the rest (not vaporized) sodium metal to sodium oxide and superoxide as appears from X-ray diffraction patterns illustrated in Fig. 2.

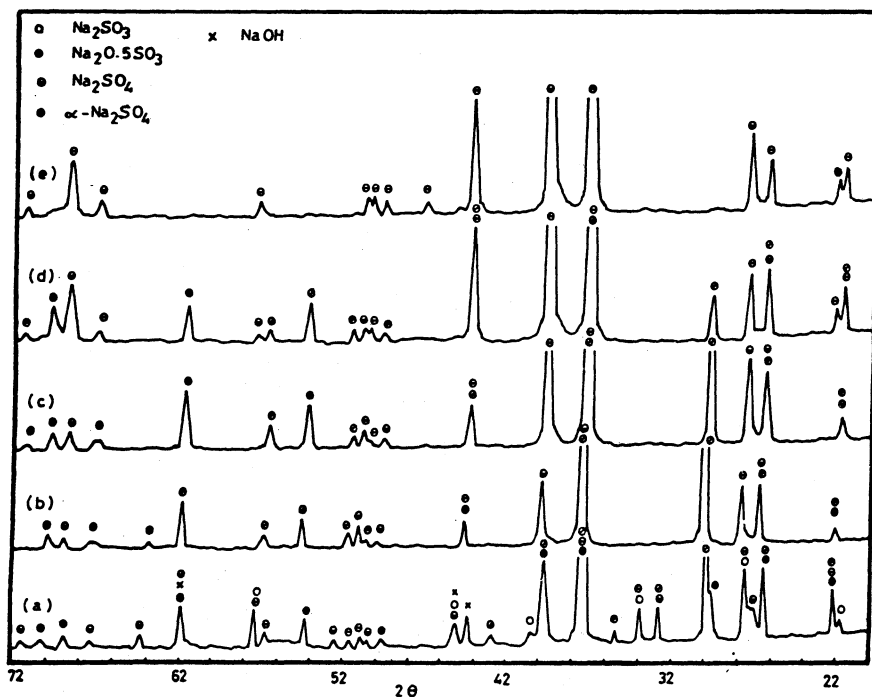
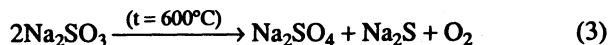


Fig. 3 X-ray diffraction patterns of products resulted from heating sodium sulfite salt at 700 (a), 800 (b), 850 (c), 900 (d) and 1000°C (e) for 4 h, using Co K α irradiation and nickel filter.

In case of the third step which lies in the range of temperature between 645 and 790°C, it can be seen that there is again a gradual weight loss which reaches maximum at 770°C and amounts to 0.8%. This loss may be attributed to the evolution of small amounts of sulfur dioxide produced as a result of interaction of sodium pentasulfate with sodium sulfide according to the following equation;



provided that sodium sulfide was produced as a result of thermal dissociation of sodium sulfite at 600°C¹⁵ according to the following equation,



The liberated sulfur dioxide (Eqn. 2) reacts with the resulted species of sodium oxide and peroxide leading to formation of a little amount of sodium sulfite as can be seen from the appearance of its characteristic X-ray diffraction patterns illustrated in Fig. 3.

From the fourth step which is concerned with the temperatures higher than 790°C it is clarified that the weight of the sample increases gradually and approaches 100% and even exceeds to *ca.* 104.5% of the weight of the sample at 1000°C. This finding may be attributed to the thermal dissociation of sodium

pentasulfate at temperature higher than 800°C to sodium sulfate and sulfur trioxide which reacts with the rest of different types of sodium oxides leading to formation of sodium sulfate.

It is known that the complete conversion of one mol of sodium sulfite to sodium sulfate is accompanied with an increase of the weight of the sample equal to 12.69% which is higher than the found value (*ca.* 4.5%). This difference which amounts to 8.20% between the theoretical value and the practical one may be attributed to volatilization of 60.70% of sodium metal formed according to equation (1) during the first step. The loss of sodium is accompanied with a loss of the corresponding stoichiometric amounts of SO₂ and SO₃ in the third step. This finding was also confirmed from the results of the work of Erdey *et al.*¹³, where it can be observed from DTG curve of sodium sulfite that the increase in weight in his sample amounts to *ca.* 8%.

The presence of reducing species such as sodium sulfide and/or sodium sulfite, in different thermal products, was also proved from their determination (together) by using the iodometric titration method¹⁷.

It was found experimentally according to the results illustrated in Fig. 4 that the rate of conversion of the sodium sulfite increases gradually by heating between 250 and 600°C whereas it increases sharply between 600 and 700°C due to conversion of the sulfite to sodium pentasulfate, in addition to conversion of the salt to the corresponding sulfate and sulfide (Eqn. 3). At temperatures higher

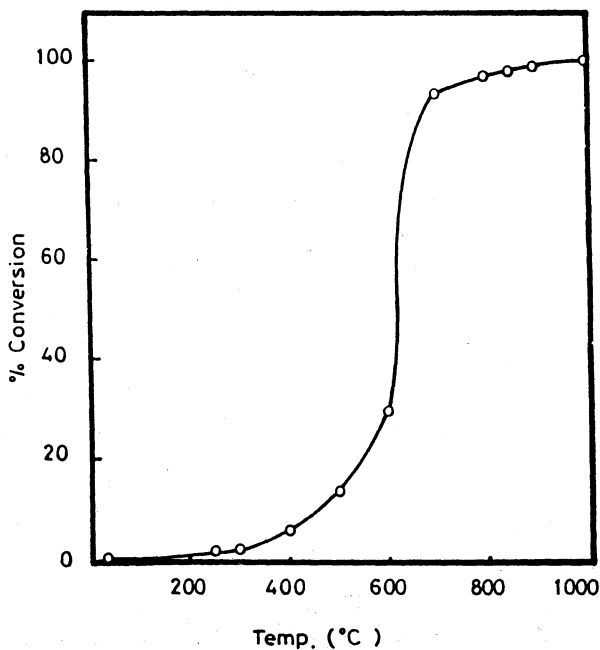


Fig. 4 Percentage of conversion of sodium sulfite to sodium hexavalent sulfur salts such as sodium sulfate and sodium pentasulfate as a result of heating the salt for 4 h at different temperatures.

than 700°C (Fig. 4), the presence of fewer percentages of reducing salts (Na_2SO_3 and Na_2S) may be attributed to the reaction between sulfur dioxide and oxides of sodium as mentioned before. The further fate of the newly formed sulfite is the same as described before, so that it was found experimentally that the percentage of the sulfite salt decreases gradually above 700°C and reaches about 0.1% at 1000°C (Fig. 4).

Conclusion

1. The oxidation process of sodium sulfite to the corresponding sulfate was found to be a complicated process and not a simple one as mentioned earlier by many investigators.
2. The complete conversion of sodium sulfite to the corresponding sulfate can be achieved by heating the sulfite salt at 1000°C for 4 h.

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