Solid State Vibrational Spectroscopy. Part 7.[1] A Vibrational Spectroscopic Study of the Thermal Decompositions of Sodium and Potassium Thiosulphate

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The thermal decompositions of $Na_2[S_2O_3]$ and $K_2[S_2O_3]$ have been studied using thermal gravimetric analysis, and by recording the i.r. and Raman spectra of the products formed when the two salts are heated to various temperatures in air and in nitrogen. The spectroscopic studies reveal the formation of polysulphides: Na_2S_2 and γ-Na_2S_5, in the case of $Na_2[S_2O_3]$, and K_2S_3, K_2S_4, and K_2S_5, in the case of $K_2[S_2O_3]$, which, in air, are subsequently oxidized to give the sulphate salt as the final product. Studies on the decomposition of solid mixtures of $Na_2[S_2O_3]$ and $Na_2[SO_3]$ show that all the $Na_2[SO_3]$ is consumed, supporting the hypothesis that sulphite is an intermediate in the decomposition.

ALTHOUGH Picon[2] suggested as long ago as 1924 that the thermal decomposition of sodium thiosulphate could proceed *via* the formation of polysulphides, more recent work[3,4] using thermogravimetric analysis (t.g.a.), differential thermal analysis (d.t.a.), and i.r. spectroscopy has been interpreted in terms of a mechanism involving the formation and subsequent oxidation of sulphite as intermediate.

$$Na_2[S_2O_3] \longrightarrow Na_2[SO_3] + S \qquad (1)$$

$$S + O_2 \longrightarrow SO_2 \qquad (2)$$

$$2Na_2[SO_3] + O_2 \longrightarrow 2Na_2[SO_4] \qquad (3)$$

In the present study we have examined the thermal decompositions of the sodium and potassium salts using t.g.a., and by recording the i.r. and Raman spectra of the products formed when the two salts are heated to various temperatures in air and in nitrogen.

RESULTS

T.G.A. Study.—The above decomposition scheme (1)—(3) would give rise to a very simple t.g.a. trace since reaction (1) does not lead to any weight loss and there would then be competition between the weight loss in reaction (2) and the weight gain in reaction (3). The trace for the potassium salt in particular (Figure 1) is very simple and both traces give the correct weight loss for the thiosulphate ⟶ sulphate conversion and could thus be interpreted as being confirmatory evidence for the above decomposition scheme.

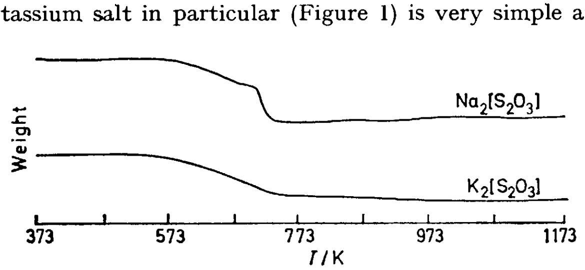

FIGURE 1 T.g.a. traces of the thiosulphate salts in air

Spectroscopic Studies.—The spectroscopic study consisted of heating samples to various temperatures in air or nitrogen and recording the i.r. and Raman spectra of the cooled products. The discussion will concentrate mainly on the Raman results since they are more informative than those of the i.r. spectra, but the latter will be commented on where appropriate.

Studies in nitrogen. Figures 2 and 3 illustrate the Raman spectra of $K_2[S_2O_3]$ and $Na_2[S_2O_3]$ after heating to 723 K (without decomposition) and of the products formed after heating to the temperatures indicated. The two main observations are as follows. (*a*) Both salts give rise to a band near 990 cm^{-1} which can be assigned[5] to the $\nu_1(a_1)$ mode of $Na_2[SO_4]$ (phase III) (996 cm^{-1}) and $K_2[SO_4]$ (984 cm^{-1}), thus indicating that sulphate can be formed *in the absence of oxygen*, which is not in agreement with the previous decomposition scheme (1)—(3). Furthermore, this is the only band observed in the 900—1 000 cm^{-1} region, no bands characteristic[6] of sulphite being observed. (*b*) More intense Raman bands are also observed in the 400—500 cm^{-1} region, which can be assigned[7-9] to various polysulphides. In the case of the potassium salt (Figure 2), the polysulphide products at 903 K are K_2S_5 (Raman bands[8] at 252m, 268w, 432s, 485w, and 496m cm^{-1}), K_2S_4 [Raman bands[8] at 220m, 266m, 434s, 478 (sh), and 485s cm^{-1}], and K_2S_3 (Raman bands[8] at 238m and 466s cm^{-1}). At 983 K the product is mainly K_2S_3 plus some K_2S_4, and at 1 103 K K_2S_3 is the only product.

In the case of the sodium salt (Figure 3) identification of the polysulphides is a bit more difficult due to the similarity of their vibrational Raman values.[9] Our interpretation of Figure 3 is that Na_2S_2, Na_2S_4, and Na_2S_5 are all formed initially but that Na_2S_2 and γ-Na_2S_5 become the predominant products at higher temperature. This indicates that the decomposition of $Na_2[S_2O_3]$ is more complicated than assumed in a recent kinetic study[10] where Na_2S_5 was considered to be the only polysulphide formed.

Studies in air. Two main differences are observed when the decompositions are carried out in air. (*a*) The samples burn readily with the formation of SO_2, whereas in nitrogen sulphur vapour (identified from the Raman spectrum[11] of the condensed vapour) is evolved from the sample at temperatures in excess of its boiling point (717 K). (*b*) At temperatures just above the decomposition temperature, polysulphides can be detected in the product, but at higher temperatures sulphate is the only product. Once again, bands characteristic of sulphite *cannot* be observed in the Raman spectra of the products. Furthermore samples previously heated in nitrogen, and thus containing polysulphides, are converted into the sulphate alone when reheated in air.

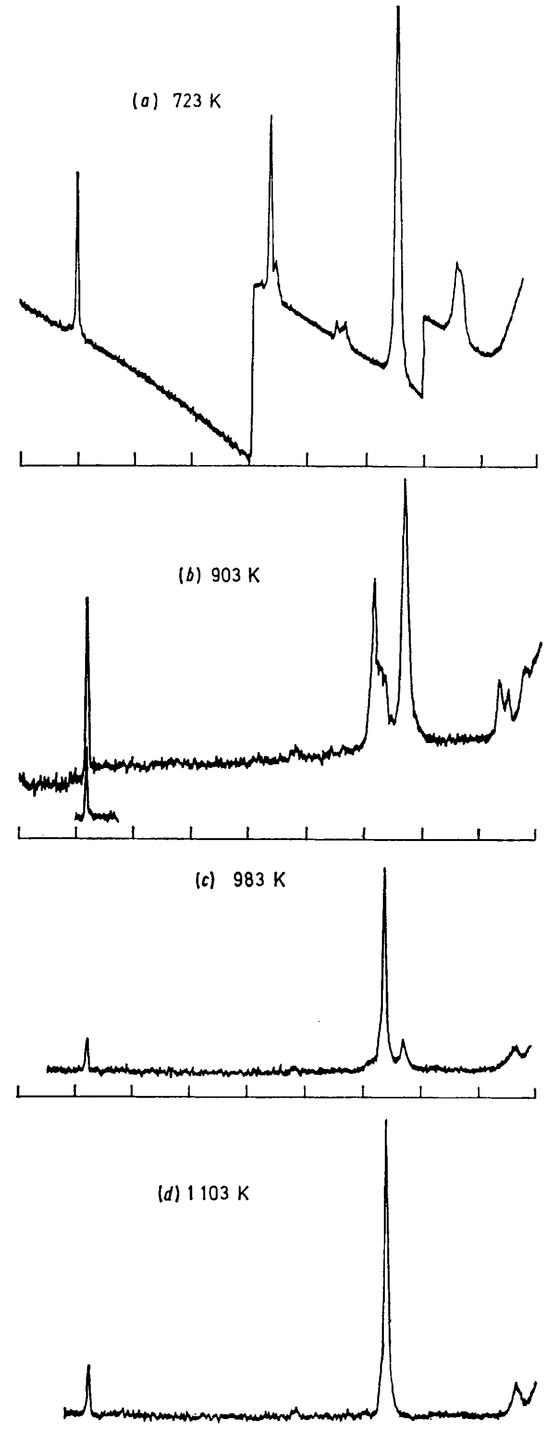

FIGURE 2 The Raman spectra of (a) $K_2[S_2O_3]$ after heating to 723 K (without decomposition), and of the thermal decomposition products (b)—(d) after heating in nitrogen at the indicated temperatures

DISCUSSION

The above observations that sulphate is formed in the absence of oxygen and that sulphur vapour is evolved can be satisfactorily accounted for by equations such as (4)—(6), whilst in the presence of oxygen, the sulphur

$$2M_2[S_2O_3] \longrightarrow 2M_2S_2 + 3O_2 \quad (4)$$

$$4M_2[S_2O_3] \longrightarrow M_2S_3 + 3M_2[SO_4] + 2S \quad (5)$$

$$4M_2[S_2O_3] \longrightarrow M_2S_5 + 3M_2[SO_4] \quad (6)$$

and the polysulphides are oxidized to the sulphate [equations (7)—(9) and (2)].

Although these equations do account for the experimental observations they do not give any indication of

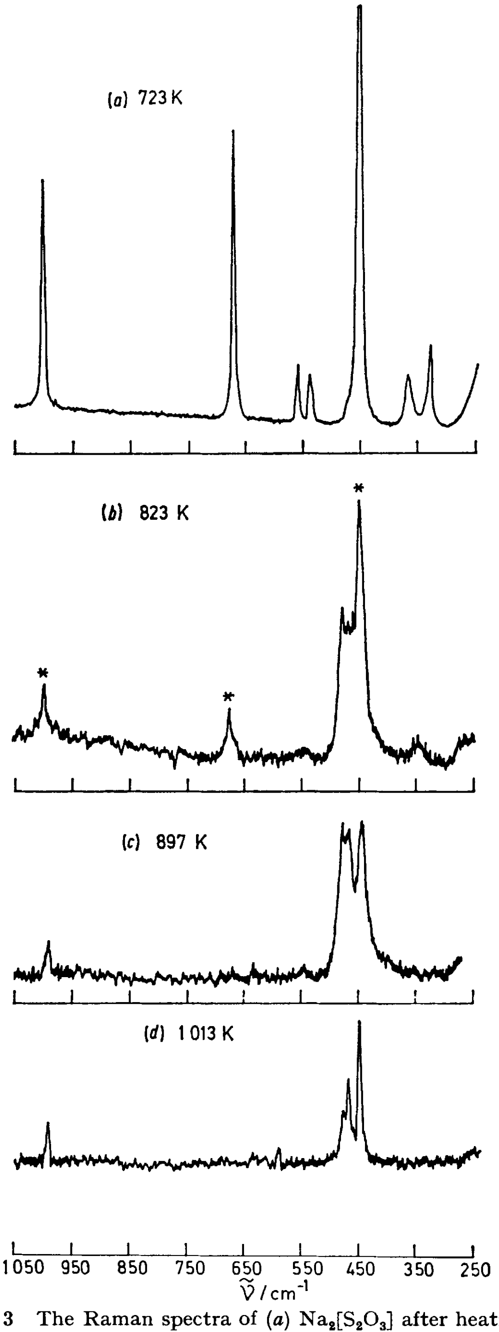

FIGURE 3 The Raman spectra of (a) $Na_2[S_2O_3]$ after heating to 723 K (without decomposition), and of the thermal decomposition products (b)—(d) after heating in nitrogen at the indicated temperatures. Bands marked with an asterisk in (b) arise from some undecomposed $Na_2[S_2O_3]$

the mechanism of the decompositions. Although we have been unable to detect the presence of sulphite as

$$M_2S_2 + 3O_2 \longrightarrow M_2[SO_4] + SO_2 \qquad (7)$$

$$M_2S_3 + 4O_2 \longrightarrow M_2[SO_4] + 2SO_2 \qquad (8)$$

$$M_2S_5 + 6O_2 \longrightarrow M_2[SO_4] + 4SO_2 \qquad (9)$$

$$S + O_2 \longrightarrow SO_2 \qquad (2)$$

intermediate from our i.r. and Raman studies, it is difficult to envisage any decomposition mechanism for thiosulphate which does not proceed *via* such an intermediate.

The non-observation of bands due to sulphite does not preclude the presence of a very low steady-state concentration of sulphite intermediate. To test this hypothesis, equimolar solid mixtures of thiosulphate and sulphite were heated to various temperatures in nitrogen and the i.r. and Raman spectra of the products recorded with the following observations: (*a*) the spectra of the products are very similar to those obtained when thiosulphate alone is heated at a similar temperature; (*b*) the spectra contain bands characteristic of sulphate and polysulphides; (*c*) *no sulphite bands* can be observed even though (*i*) they are easily observable in the spectra of the initial equimolar solid mixtures, (*ii*) when heated in nitrogen the sulphite salts alone remain unchanged.

These observations suggest that all the sulphite has been consumed indicating that it is indeed an intermediate in the decomposition.

There are two main reasons why the previous i.r. study [4] failed to detect the presence of polysulphides but favoured reaction scheme (1)—(3). (*a*) The lower limit of the study was 650 cm^{-1} which precluded observation of the polysulphide bands. (*b*) Samples of $Na_2[S_2O_3]$ heated in nitrogen gave an i.r. band at 965 cm^{-1} which was assigned to the $\nu_3(e)$ mode of $[SO_3]^{2-}$. We confirm the existence of this band but it is now clear that this was an erroneous assignment and that the band should have been assigned to the overtone of the ν(S–S) mode of polysulphide.

In summary the present study has shown that the decompositions of thiosulphate salts involve the formation of various polysulphides *via* the sulphite intermediate.

EXPERIMENTAL

AnalaR samples were used when available without further purification. The t.g.a. traces were run by Dr. M. B. Davies at Stockport College of Technology on a Stanton TR-1 thermobalance using a heating rate of 4° min^{-1}. The decomposition studies were carried out by inserting samples of the thiosulphate salts, contained in a porcelain boat, into a preheated furnace for 5 min whilst purged with air or nitrogen.

The Raman spectra were excited using either the 514.5 nm line of a CRL CR-4 Ar^+ laser for white samples or the 586.8 nm line of a CR-590 dye laser containing rhodamine-6G and pumped by the Ar^+ laser, for coloured samples. The spectra were recorded on a Cary 81 spectrometer converted into a 90° sampling arrangement by Anaspec Ltd. The samples were contained in spinning sample tubes and the spectra recorded using 3 cm^{-1} slit widths. Infrared spectra of KBr discs in the range 250—2 000 cm^{-1} were recorded on a PE 225 spectrometer which was calibrated using a polystyrene film.

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