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Identification of the Products of the Reaction between Sulfur and Sodium Carbonate

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Introduction

It is well-known[1−5] that heating a mixture of sodium (or potassium) carbonate with sulfur leads to the formation of polysulfides with evolution of CO_2 at 260−280 °C.[4,5] However, this reaction has not been investigated in detail, nor have the products identified, except CO_2. Several equations have been proposed for the reaction between sulfur and carbonate. According to Satava,[2] it leads to the formation of sodium tetrasulfide (Na_2S_4) and sodium thiosulfate ($Na_2S_2O_3$):

$$3Na_2CO_3 + 10S \rightarrow 2Na_2S_4 + Na_2S_2O_3 + 3CO_2 \tag{1}$$

Kanatzidis[3] has proposed a general equation for the reaction between carbonate and sulfur which suggests that several polysulfides could be synthesized, depending on the sulfur/carbonate ratio:

$$3K_2CO_3 + 2(x + 1)S \rightarrow 2K_2S_x + K_2S_2O_3 + 3CO_2 \tag{2}$$

More recently,[4] the reaction occurring at 350 °C has been described by the equation

$$2Na_2CO_3 + 7S \rightarrow {}^5/_4Na_2S_5 + {}^3/_4Na_2SO_4 + CO + CO_2 \tag{3}$$

In this paper,[4] it is claimed, from IR spectroscopy experiments, that a small amount (≈2%) of COS has been detected in the evolved gas.

The reaction between sulfur and sodium carbonate can be interpreted as the redox disproportionation of sulfur leading to the formation of reduced species and of oxidized species of sulfur. Up to now, the chemical species involved in this reaction have not been clearly identified. In the present communication, we report a detailed investigation of the reaction between sulfur and sodium carbonate. The weight loss of the mixture after heating at 350 °C has been measured, and the reaction products have been identified by Raman and IR experiments.

It must also be mentioned that $Na_2S_2O_3$ is disproportionated at high temperature. For Satava,[2] the disproportionation of $Na_2S_2O_3$ occurs at 450 °C, giving Na_2S_5 and Na_2SO_4. However, several authors[4−8] suggest other disproportionation reactions of $Na_2S_2O_3$. In the present paper, we shall also consider this point.

Experimental Section

Anhydrous sodium carbonate (Fluka, >99%) and sublimed sulfur (Fluka, >99.999%) are weighed in order to obtain given S/Na_2CO_3 mole ratios. These reactants are ground and carefully mixed, and a mass of about 100 g is introduced into a reaction tube (Pyrex, 20 mm inner diameter). After the filling, the reaction tube is weighed. Then, it is connected to a mercury manometer, introduced into a tubular furnace, and smoothly heated. The pressure inside the reaction tube is allowed to increase up to about 300 mmHg; when this pressure is reached, gas is evolved and the pressure inside the tube remains constant. From about 260 °C, CO_2 is evolved from the reaction mixture. The temperature of the tube is then increased very slowly up to about 300 °C, in order to keep the gas evolution at a very slow rate. This process lasts for about 2 h. After this period, there is almost no more gas evolution, and the furnace is heated to 350 °C and maintained at this temperature for about 12 h. After cooling down to the room temperature, the reaction tube is weighed (without any introduction of air into the tube). The difference with the weight before heating corresponds to the weight loss of the reaction mixture of sodium carbonate and sulfur and is assigned to the evolution of CO_2. It must be emphasized that, because of the very slow heating rate between 260 and 300 °C, the sulfur vapor loss is negligible. These sulfur vapors are condensed on the cold surface of the reaction tube outside the furnace, so that no weight loss can be assigned to the loss of sulfur.

The reaction products of the heating experiment are taken out of the reaction tube in a glovebox, ground, and put in glass tubes (4 mm inner diameter) which are sealed under vacuum.

Raman spectra, obtained with the 457.9 nm excitation line of an argon laser, were recorded with a RT30 Dilor spectrometer at room temperature. The samples were rotated during the experiments, and the power of the radiation line was kept below 75 mW. The IR spectra were obtained with an FT1600 Perkin-Elmer spectrometer by transmission experiments using KBr pellets.

Results

The weight loss of the mixtures was analyzed by assuming that it was due to the evolution of CO_2. Consequently, the weight loss gives the number of Na_2CO_3 molecules which have reacted with sulfur. Figure 1 displays the variation of the number of moles of evolved CO_2/mol of Na_2CO_3 introduced into the mixture versus the mole ratio $R = S/Na_2CO_3$ defining the initial composition of the heated mixture. Figure 1 shows that, for R larger than 4, the weight loss levels off, indicating the complete decomposition of carbonate. For values of R lower than about 3, a linear variation is observed, with a slope close to 1/3.33, indicating that 10 mol of sulfur reacts with 3 mol of Na_2CO_3. According to eq 1, the disproportionation reaction of sulfur in the presence of carbonate could lead to the formation of the tetrasulfide ion S_4^{2-} and of thiosulfate. Our result corresponds to the stoichiometry of the equation of the reaction suggested by Satava.[2]

In order to check the hypothesis that thiosulfate and tetrasulfide are formed, the Raman spectra of the reaction products were recorded, at room temperature, for various compositions of the reaction mixture. For mixtures with R lower than 3, the four more intense bands of the recorded Raman spectra (Figure

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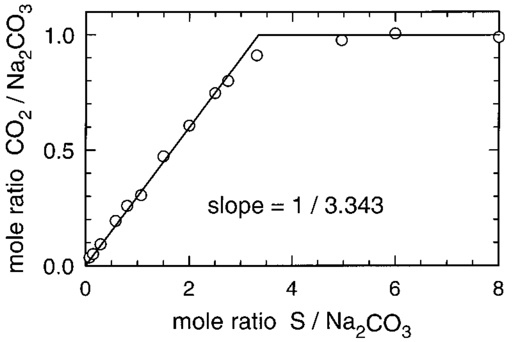

Figure 1. Variation of the mole ratio of evolved CO_2 per Na_2CO_3 introduced in the mixture of sulfur and sodium carbonate versus the S/Na_2CO_3 mole ratio defining the composition of the initial mixture. The mixtures were heated at 350 °C for about 12 h. The entire weight loss has been assigned to the evolution of CO_2.

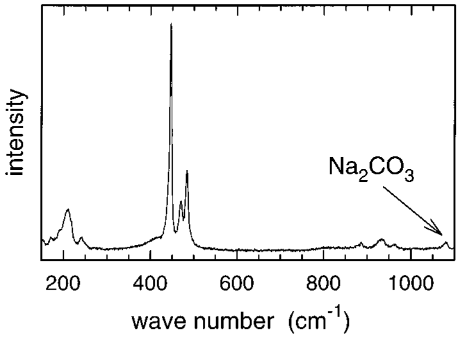

Figure 2. Raman spectrum, recorded at room temperature with the 457.9 nm excitation line, of an $S_8 + Na_2CO_3$ mixture (molar ratio $S/Na_2CO_3 = 1.07$) after heating at 350 °C.

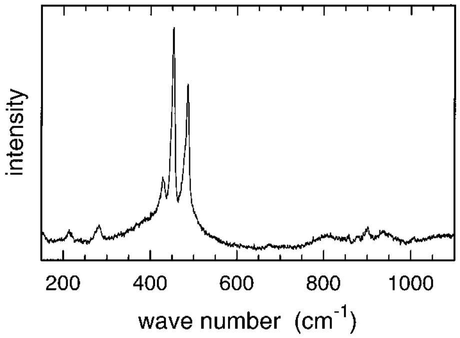

Figure 3. Raman spectrum, recorded at room temperature with the 457.9 nm excitation line, of an $S_8 + Na_2CO_3$ mixture (molar ratio $S/Na_2CO_3 = 3.3$) after heating at 280 °C.

2) are located at 210, 445, 470, and 485 cm^{-1}. They are assigned to S_4^{2-} in the definite compound Na_2S_4, by comparison with the Raman spectrum published by Janz et al.,[10] and with the Raman spectrum of Na_2S_4 synthesized in our laboratory by reaction between stoichiometric amounts of sodium and sulfur in liquid ammonia. A Raman band is also observed at 1080 cm^{-1}, which must be assigned to Na_2CO_3. This band is observed in all the mixtures with *R* lower than 3, showing that sodium carbonate has not completely reacted in these mixtures and is in excess. This result is in agreement with the stoichiometry of eq 1.

For mixtures with *R* larger than 3.3, the recorded Raman spectra (Figure 3) are close to that of S_5^{2-} in the definite compound Na_2S_5.[10] For all mixtures with *R* larger than 3.3, the Raman band of CO_3^{2-} at 1080 cm^{-1} is not observed, indicating that sodium carbonate has completely reacted. Furthermore, in mixtures with *R* larger than about 6, the Raman bands of sulfur S_8 are observed, in addition to those of Na_2S_5.

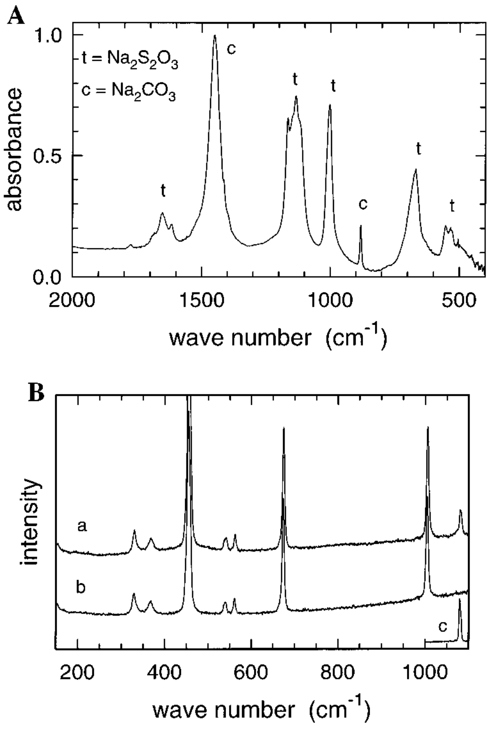

Figure 4. Spectra, recorded at room temperature, of an $S_8{-}Na_2CO_3$ mixture (molar ratio $S/Na_2CO_3 = 3.3$) after heating at 280 °C and washing with ethanol. (A) IR spectrum. The vibration bands of sodium carbonate and thiosulfate are indicated. (B) Raman spectra: (a) spectrum of the mixture; (b) spectrum of anhydrous sodium thiosulfate; (c) spectrum of sodium carbonate.

The Raman spectra (Figures 2 and 3) confirm the analysis of the weight loss measured for the various heated mixtures: sodium carbonate is in excess for *R* lower than 3.3. The Raman spectra also show that, when sodium carbonate is in excess, the reaction between sulfur and sodium carbonate leads to the formation of only one polysulfide, S_4^{2-}, whatever the composition of the mixture is. When sulfur is in excess, *i.e.* when *R* is larger than 3.3, the excess sulfur reacts with the S_4^{2-} ion initially formed, probably leading to other polysulfides S_n^{2-} ($n > 5$). However, it should be emphasized that, after cooling down at room temperature, only the bands of S_5^{2-} are observed in the Raman spectra (Figure 3). This observation is in agreement with the phase diagram of the sodium−sulfur system,[9] which shows that, in addition to Na_2S and Na_2S_2, the only definite compounds existing in the solid state are Na_2S_4 and Na_2S_5. The observation of S_4^{2-} and S_5^{2-} at room temperature does not prove that they are the only polysulfide ions present in the mixtures at 350 °C, because these ions could be partly disproportionated or dissociated at this temperature. For samples sealed under vacuum with the overall composition Na_2S_4 and Na_2S_5, heated at 550 °C and cooled very rapidly at the temperature of liquid nitrogen, the same anisotropic ESR signal is observed as for samples of overall composition Na_2S_6.[11] This ESR signal is characteristic of the polysulfide S_3^-. The observation of the S_3^- radical in these quenched samples proves the partial

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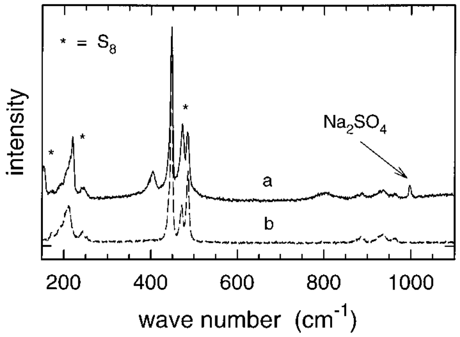

Figure 5. Raman spectrum, recorded at room temperature, of anhydrous sodium thiosulfate heated under vacuum at 550 °C during 7 h. Spectrum a is assigned to the sum of the contribution of S_4^{2-} (spectrum b), of sulfur S_8 (*), and of sodium sulfate.

disproportionation of S_4^{2-} and S_5^{2-} at high temperature. However, we have not determined the temperature at which the disproportionation of S_4^{2-} and S_5^{2-} appears or the extent of this disproportionation.

The Raman spectra (Figures 2 and 3) of the product of the reaction between sodium carbonate and sulfur do not display any band which could be assigned to an oxidized species of sulfur. We have shown that is a consequence of the low sensitivity of the Raman bands of $Na_2S_2O_3$ compared with the sensitivity of the polysulfide bands under the experimental conditions which have been used. An equimolar mixture of anhydrous Na_2S_4 and $Na_2S_2O_3$ was prepared (ground and mixed in a glovebox and introduced into a Pyrex tube which was then sealed under vacuum). In the Raman spectrum of this mixture, recorded under the 457.9 nm excitation line, the Raman bands of the $S_2O_3^{2-}$ anion are about 50 times less intense than the Raman band of S_4^{2-} at 450 cm^{-1}. Consequently, we cannot expect to find evidence of sodium thiosulfate in the Na_2S_4–$Na_2S_2O_3$ mixture with a 2/1 molar ratio, predicted by eq 1. In order to identify the oxidized form of sulfur resulting from the reaction between sulfur and sodium carbonate, the reaction product was washed in ethanol, a solvent in which polysulfides are highly soluble but sodium thiosulfate and sodium carbonate are almost insoluble.[12] A white solid was then obtained. Its IR and Raman spectra display the vibration bands of CO_3^{2-} and $S_2O_3^{2-}$ (Figures 4 for $R = 3.3$) by comparison with the Raman spectra of the pure corresponding compounds we have recorded. This shows that, under the experimental conditions we have used for heating the mixture of sodium carbonate with sulfur (i.e., at 350 °C), the oxidized form of sulfur is sodium thiosulfate, as expected from eq 1.

According to several authors, sodium thiosulfate is unstable and is irreversibly disproportionated at high temperatures.[2,4-8] However, these authors give different temperatures of decomposition: 223 °C, Choi et al.;[4] 450 °C, Satava.[2] The products of this decomposition were not unambiguously identified: two authors suggest sulfite and sulfur,[6,7] and others, sulfate and polysulfides.[2,4,5] In order to clarify this point, anhydrous sodium thiosulfate (Fluka), in tubes sealed under vacuum, was heated at various temperatures and the Raman spectra were recorded at room temperature (without the opening of the tubes). These experiments show that sodium thiosulfate is stable under heating at 280 °C during 14 h. After heating at 550 °C during 7 h, sodium thiosulfate is fully decomposed into Na_2S_4, sulfur S_8, and Na_2SO_4 (Figure 5). We have not accurately determined the temperature of the beginning of the disproportionation of the thiosulfate, but it increases rapidly for temperatures higher than about 400 °C. The Raman band of SO_4^{2-} is weak compared to the Raman bands of S_4^{2-}. However, these relative intensities can be assigned to a sulfate/tetrasulfide molar ratio close to 1, as we have checked for an equimolar mixture of Na_2S_4 and Na_2SO_4 prepared in a glovebox and introduced into a tube sealed under vacuum. As a consequence of the chemical species observed, the following equation can be proposed for the irreversible disproportionation of sodium thiosulfate at high temperature:

$$4Na_2S_2O_3 \rightarrow Na_2S_4 + {}^1/_8S_8 + 3Na_2SO_4 \tag{4}$$

Conclusion

The products of the reaction between sodium carbonate and sulfur at 350 °C have been identified at room temperature by using Raman and IR spectroscopies. The reaction begins at 260 °C. It has been verified, for several compositions of the mixture, that the results would have been the same if the mixtures had been heated at 280 °C. When sodium carbonate is in excess (mole ratio $S/Na_2CO_3 < 3.3$), only one polysulfide, S_4^{2-}, is formed, but when sulfur is in excess, only S_5^{2-} is observed. In all cases, the reaction is a disproportionation reaction of sulfur, and sodium thiosulfate is the oxidized form of sulfur. The disproportionation of sodium thiosulfate is shown to be negligible at 350 °C. The more remarkable point of these results is that S_4^{2-} is the only formed polysulfide when there is no excess of sulfur.

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