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HIGH TEMPERATURE REACTIONS OF TITANIUM(IV) OXIDE WITH SOME ALKALI PERSULFATES AND THEIR DECOMPOSITION PRODUCTS

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ABSTRACT

The solid state reactions between TiO_2 and $Na_2S_2O_8$ or $K_2S_2O_8$ have been investigated using TG, DTG, DTA, IR, and X-ray diffraction studies in the range of 20 to 1000°C.

It has been shown that TiO_2 reacts stoichiometrically (1:1) with $Na_2S_2O_8$ in the range of 160 and 220°C forming the complex sodium monoperoxodisulfato–titanium(IV) as characterized by IR and X-ray analysis. The new complex then decomposes into the reactants above 190°C.

An exothermic reaction has been observed between TiO_2 and molten $K_2S_2O_7$ at mole ratio 1:2, respectively and higher, in the range of 280 and 350°C. The IR and X-ray analyses have shown the formation of a complex namely, potassium tetrasulfato titanium(IV) for which the formula and structure have been proposed. This complex decomposes at higher temperatures into K_2SO_4 and a mixed sulfate of potassium and titanium. The mixed sulfate melts at 620°C and decomposes into K_2SO_4, TiO_2, and the gaseous SO_3.

On the other hand, $Na_2S_2O_8$ decomposes in a special mode producing a polymeric product of $Na_{10}S_9O_{32}$. Decomposition of this species occurs after melting at 560°C into Na_2SO_4 and sulfur oxides. The decomposition reaction has been proved to be catalysed by TiO_2 itself.

INTRODUCTION

Several authors[1–8] have reported on the effect of transition metal oxides on the thermal decomposition of oxo-salts. According to them the reaction depends on the nature of the oxides themselves and the oxo-salts under investigation. Moreover, with alkali persulfates, which decompose first into the pyrosulfate and then into the sulfate[9], the metal oxides may show a different behaviour towards the decomposition processes and the decomposition products. A mechanism has been suggested for the thermal decomposition of alkali pyrosulfates in the presence of nickel(II) oxide[10].

In this piece of research the reaction of titanium(IV) oxide with sodium and potassium persulfates and their decomposition products are investigated using such techniques as thermogravimetry, differential thermal analysis, IR, and X-ray diffraction analysis.

EXPERIMENTAL

Materials

All materials were analytical grade.

Apparatus and Methods

TG, DTG, DTA graphs were recorded using a Paulik–Paulik–Erdey MOM derivatograph. The general procedure followed in mixing and analysis of TiO_2–$Na_2S_2O_8$ and TiO_2–$K_2S_2O_8$ systems was described elsewhere[9, 10].

The IR spectra were developed by Perkin–Elmer Infracord IR spectrophotometer No. 137E. The samples were analysed as KBr discs.

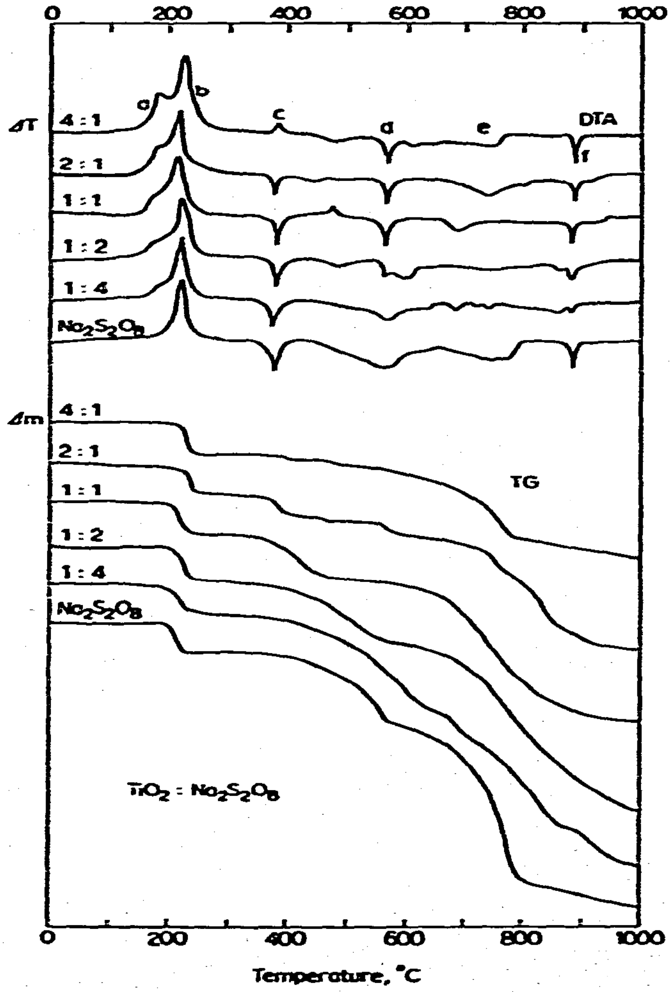

Fig. 1. TG and DTA curves of titanium (IV) oxide–sodium persulfate mixtures.

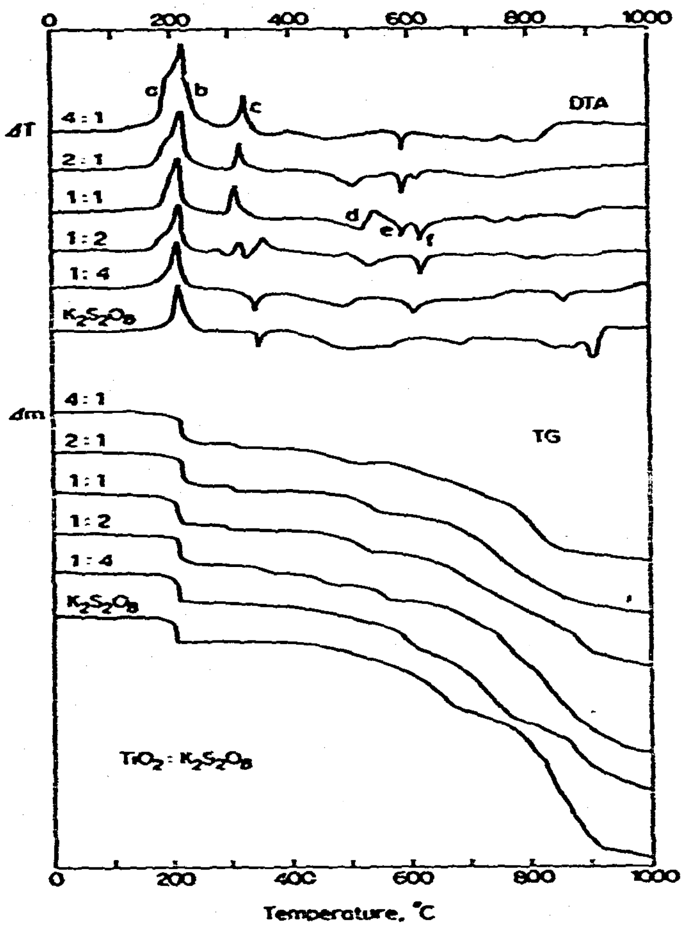

Fig. 2. TG and DTA curves of titanium(IV) oxide-potassium persulfate mixtures.

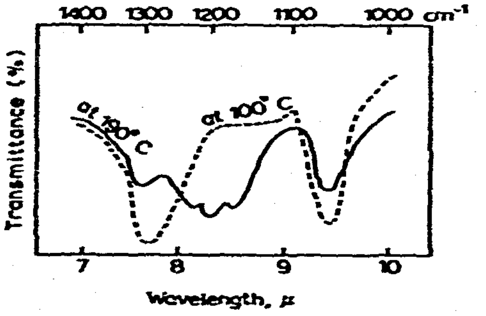

Fig. 3. IR spectra of 1:1 molar mixture of titanium(IV) oxide with sodium persulfate at 100°C (---); and at 190°C (——).

The X-ray diffraction analyses were carried out in a Philips 1410 X-ray diffractometer using copper tube at 30 mA and 40 KV. The lines were referred to the Cu-Kα line.

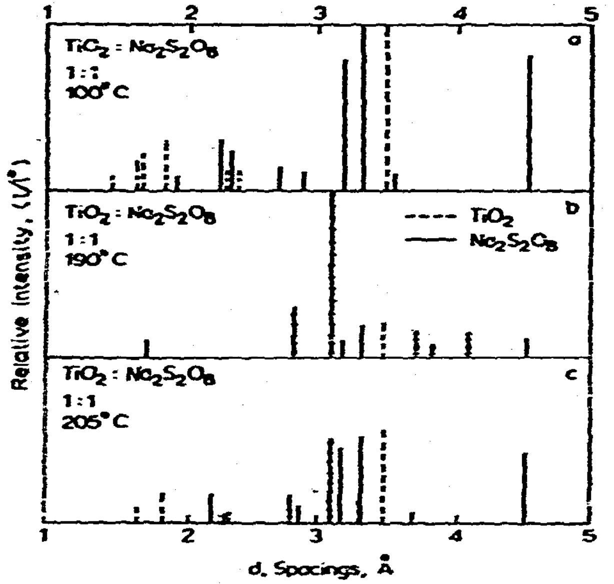

Fig. 4. X-ray diffraction patterns of 1:1 molar mixture of titanium(IV) oxide with sodium persulfate at 100°C (a); 190°C (b); and 205°C (c).

RESULTS AND DISCUSSION

Figures 1 and 2 show the derivatograms of sodium persulfate and potassium persulfate mixtures with titanium(IV) oxide at oxide/persulfate mole ratios of 1:4, 1:2, 1:1, 2:1, and 4:1, respectively.

The DTA curves of Figs. 1 and 2, step a, indicate an exothermic process takes place in the range* of 160 and 220°C with a maximum peak temperature at 187°C (obtained from the derivatograms of sodium persulfate mixtures). Better resolution of this peak is obtained with higher mole ratios. In order to provide an interpretation for this exotherm, the samples of the reaction mixtures after heating to 100, 190, and 205°C were analysed by IR and X-ray diffraction. Figure 3 shows the IR spectra of the reaction mixture at 100, and 190°C. The IR spectrogram (a) represents the absorption bands of the persulfate[11]. The main peaks are located at 1059.3, 1265.8, and 1290.3 cm^{-1} where the first one is found to be characteristic of most oxo-sulfur compounds with oxygen bridging as in the case of persulfate and pyrosulfate. TiO_2, on the other hand, absorbs[12] in a region beyond 700 cm^{-1}, and therefore causes no interferences. After heating to 190°C the intensity of these bands decreases, while new bands appear at 1216.6, 1190, and 1141.7 cm^{-1}. This indicates that the persulfate reacted with titanium(IV) oxide forming a new compound. In an attempt to identify the compound formed, the samples were examined by X-ray diffraction (Fig. 4). As with the IR spectrum, it can be shown that the lines due to $Na_2S_2O_8$ (3.32 Å) and TiO_2 (3.51 Å) decrease in intensity whereas new lines appeared at 4.14, 3.97, 3.925,

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* The figures are obtained by resolving the peaks graphically.

3.738, 3.13, 2.84, and 2.686 Å, the strongest line being at 3.13 Å. This confirms the IR spectrum in that a reaction between sodium persulfate and titanium(IV) oxide has occurred with the result of new species formation. Reference to the A.S.T.M. cards did not help in identifying the new product. The most probable compounds which might have been formed are peroxotitanium(IV) compounds, since the element is characterised by its ability to form such compounds[13, 14]. The most probable products are, TiO_3, $Ti(O_2)SO_4$, or $Na_2[Ti(O_2)(SO_4)_2]$.

The formation of TiO_3 would require the abstraction of one oxygen atom from the persulfate to combine with TiO_2 giving TiO_3. In this case the formation of $Na_2S_2O_7$ would be a stoichiometric requirement. However, the X-ray pattern does not show any lines characteristic of the sodium pyrosulfate and therefore the probability of formation of TiO_3 would be ruled out.

The formation of $Ti(O_2)SO_4$, requires not only the formation of the pyrosulfate but also further decomposition to the sulfate. Again the X-ray pattern shows the absence of any lines characteristic of Na_2SO_4 and thus this probability would also be ruled out.

The third possible compound, namely $Na_2[Ti(O_2)(SO_4)_2]$ sodium monoperoxo-disulfatotitanium(IV) complex, is the most probable product. The hydrated form of this complex has been isolated from aqueous medium[15, 16], and could be formed under the present experimental conditions as anhydrous by the reaction of TiO_2 and $Na_2S_2O_8$ in a molar ratio of 1:1.

$$TiO_2 + Na_2S_2O_8 \quad \underset{> 190°C}{\overset{< 190°C}{\rightleftharpoons}} \quad Na_2[Ti(O_2)(SO_4)_2] \qquad (1)$$

At 205°C, however, the pattern shows a decrease in the peroxocompound and a corresponding increase in TiO_2 and $Na_2S_2O_8$. This indicates that the reaction is reversed at temperatures higher than 190°C.

The regenerated sodium persulfate then decomposes in the normal mode into sodium pyrosulfate, as being indicated by the IR and X-ray diffraction pattern of the product.

In the case of potassium persulfate the reaction does not proceed to completion as in the case of the sodium salt, because the potassium persulfate decomposes rapidly at 200°C. This explains the appearance of the reaction exothermic peak only as a shoulder of the peak corresponding to persulfate decomposition as compared with the clearly resolved peak in the case of sodium persulfate.

$TiO_2 : K_2S_2O_7$ system

The derivatograms of $TiO_2 : K_2S_2O_8$ mixtures, Fig. 2, indicate an exothermic process at the DTA curves, step c, accompanied by a slight but sharp weight loss, 1.2%, at TG curves, step c, between 280 and 350°C. With mole ratio 1:2 (oxide to persulfate) the corresponding exothermic peak is divided by the pyrosulfate fusion endotherm, while at higher mole ratios, 1:1, 2:1, and 4:1, the process was indicated

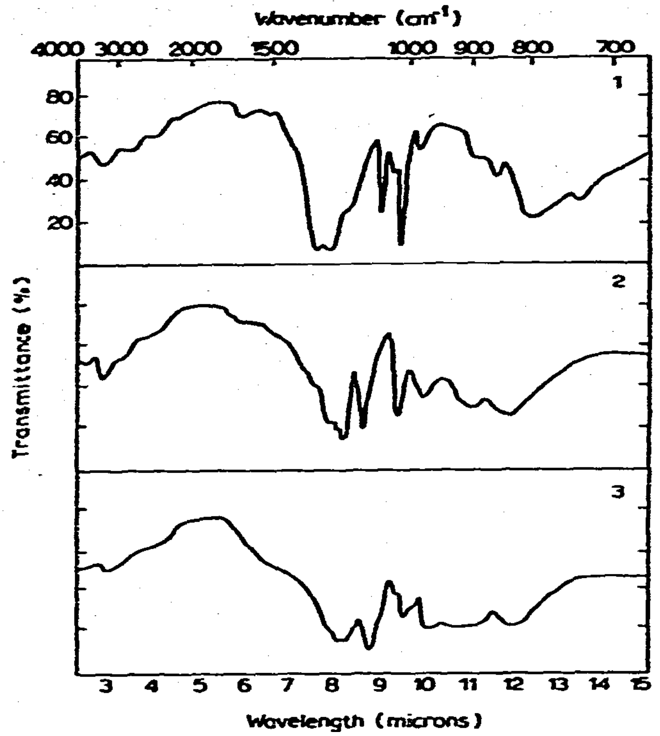

Fig. 5. IR spectra of 1:1 molar mixture of titanium(IV) oxide with potassium persulfate at 250°C (1); 350°C (2); and 580°C (3).

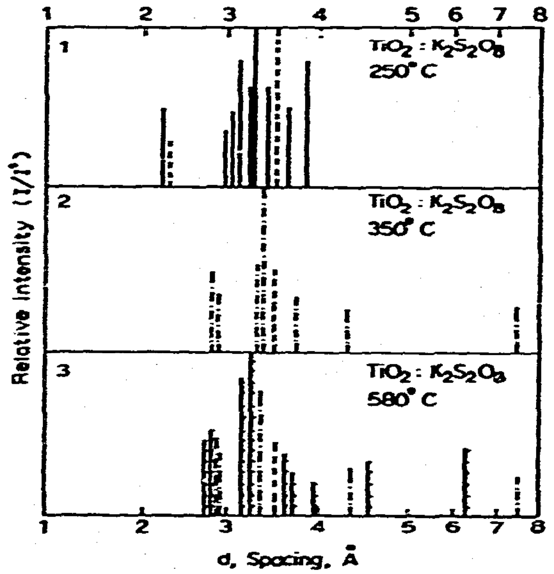

Fig. 6. X-ray diffraction patterns of 1:1 molar mixture of titanium (IV) oxide with potassium persulfate at 250°C (1); 350°C (2); and 580°C (3).

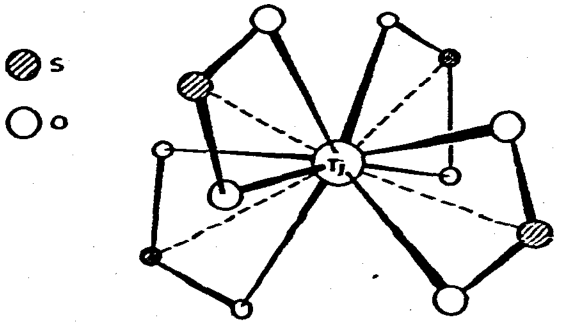

Fig. 7. The dodecahedral structure proposed for the $[Ti(SO_4)_4]^{-4}$ where two oxygen atoms are shown from each SO_4 group.

by a unique exothermic peak. The peak extends sharply upwards with a maximum peak temperature depending on the proportion of TiO_2 in the reaction mixture; being 298 °C at 1 : 1, 310 °C at 2 : 1, and 318 °C at 4 : 1 mole ratio.

In Fig. 5, IR spectrum (1) corresponds to potassium pyrosulfate since titanium(IV) oxide absorbs in a region below 700 cm^{-1}, while spectrum (2) corresponds to the reaction product of the 1 : 1 molar mixture after being heated to 350 °C. Spectrum (2) was found to be quite different from spectrum (1), which makes the formation of a new compound evident. The bands due to the new product are at 1207.7, 1133.6, 1059.1, 955, 909.0, 892.0, and 833.3 cm^{-1}. Figure 6 shows the diffraction patterns of the 1 : 1, TiO_2 : $K_2S_2O_8$ after being heated to 250, 350, and 580 °C. From pattern (2) it is clear that the diffraction lines corresponding to potassium pyrosulfate disappeared completely, while those corresponding to titanium(IV) oxide exhibited a decrease in intensity as much as one half that recorded at 250 °C. At the same time new diffraction lines show up at 350 °C indicating the presence of a new phase confirming the IR spectra of Fig. 5. In this reaction potassium pyrosulfate and titanium(IV) oxide participate in the mole ratio 2 : 1, respectively. The diffraction lines displayed by the new product are 7.505, 4.30, 3.85, 3.35, 3.28, 3.00, 2.84, 2.80, and 1.89 Å, the most intense lines being at 3.35 and 3.28 Å.

An evidence that the reaction is bimolecular with respect to potassium pyrosulfate is the shifting of the peak temperature to higher values as the amount of TiO_2 in the mixture increases, vide ultra, i.e., excess oxide will act as a diluent to the pyrosulfate.

The X-ray examination has shown that none of the known titanium(IV) sulfates namely $Ti(SO_4)_2$ or $TiOSO_4$ are present in the reaction products. It shows also that no potassium sulfate is present. One of the possible compounds which might have been formed is the complex potassium tetrasulfatotitanium(IV), $K_4[Ti(SO_4)_4]$. In the anionic part of this complex the titanium atom may be surrounded by four bidentate SO_4 groups each being linked through two oxygen atoms to the titanium atom. The structure of this anionic titanium complex may be analogous to that given for the volatile tetranitratotitanium(IV)[17] by Garner and Wallwork[18] to be a special case of dodecahedral structure (Fig. 7). The SO_4 groups are disposed so that the sulfur atoms form a slightly distorted tetrahedron. The suggested reaction product conforms with the stoichiometric requirements, since two moles of potassium pyrosulfate and one mole of titanium(IV) oxide are involved in the formation of the complex

$$TiO_2 + 2K_2S_2O_7 \rightarrow K_4[Ti(SO_4)_4] \qquad (2)$$

The IR spectrum of the product includes the bands corresponding to the sulfate as a bidentate ligand[19]. The oxygen bridging band observed in the tetranitrato-titanium(IV) spectrum[17] has also been noticed in the present case at 909 cm^{-1} being 8 cm^{-1} shifted from that of the nitrato complex. The absence of the Ti–O double bond peak, 1007 cm^{-1}, may support the existence of Ti–O coordination bonds only.

At 592°C the DTA curve of Fig. 2, step e, shows the endothermic peak corresponding to the phase transition α–β of potassium sulfate[20]. This observation leads to the existence of K_2SO_4 as a separate phase. The X-ray diffraction pattern confirms this observation and many diffraction lines related to K_2SO_4 have been recorded besides the reduction in the intensity of the lines recorded at 350°C.

The complex potassium tetrasulfatotitanium(IV), therefore, decomposes up to 580°C into potassium sulfate and another species which is mainly a mixed sulfate of potassium and titanium. The DTA curve (Fig. 2) indicates that melting of this mixed sulfate takes place at 620°C.

Above 620°C the mixed potassium-titanium sulfate decomposes into potassium sulfate, K_2SO_4, and titanium(IV) oxide evolving sulfur trioxide to the atmosphere. It is interesting to point out that at higher TiO_2 proportions the decomposition process took place at a smaller temperature intervals.

TiO_2 : $Na_2S_2O_7$ system

In the case of sodium pyrosulfate; the reaction does not take place in the same manner as with potassium pyrosulfate for two reasons, firstly, the melting occurs at a higher temperature, and secondly, the pyrosulfate properties are not preserved after melting because decomposition occurs immediately. However, in the early stages of decomposition, there is a little chance for the molten sodium pyrosulfate to react with titanium(IV) oxide. The TG curve (Fig. 1, step d) indicates that sodium pyrosulfate decomposes at lower temperatures as the amount of TiO_2 increases in the mixture upto a mole ratio of 1:1. At this mole ratio the pyrosulfate decomposition begins at 320°C, compared with 380°C for the decomposition of the pure salt. The DTA curves (Fig. 1, step c) indicate that the melting temperature of $Na_2S_2O_7$ remains unaltered whatever the amount of the oxide present in intimate admixture with the pyrosulfate. Thus the sodium pyrosulfate decomposition in the 1:4, 1:2, and 1:1 mole ratios begins already in the solid state. The decomposition proceeds in a manner different from that of the pure salt. The TG curves after about 20% of the decomposition, show a horizontal plateau extending for a considerable interval of temperature depending on the amount of TiO_2 present. The reaction product of 1:1

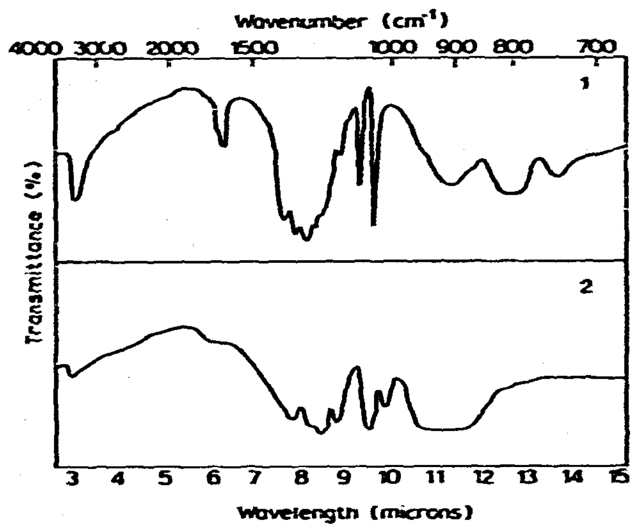

Fig. 8. IR spectra of 1 : 1 molar mixture of titanium(IV) oxide with sodium persulfate at 250°C (1); and 500°C (2).

mole ratio has been examined by IR and X-ray diffraction analysis. In Fig. 8 the IR spectrum of the reaction mixture at 250°C, spectrum 1, corresponds to sodium pyrosulfate, while that of the mixture heated to 500°C, spectrum 2, shows absorption bands different from those of sodium pyrosulfate. The absorption bands shown by the reaction products are located at 1261.2, 1242.2, 1172.3, 1142.8, 1059.6, 1002.0, and a wide band extending from 947.8 to 851.0 cm^{-1}. The spectrum indicates the existence of a new distinct phase other than sodium pyrosulfate. At first, it was thought, however, that a reaction takes place between TiO_2 and $Na_2S_2O_7$, but when the product was subjected to X-ray analysis, the diffraction pattern showed that the lines corresponding to $Na_2S_2O_7$ disappeared completely, while those corresponding to TiO_2 remain unchanged. The reaction, therefore, has nothing to do with TiO_2 and it is mainly a change involving sodium pyrosulfate. The analysis of TG curves indicates that, in the presence of titanium(IV) oxide, sodium pyrosulfate decomposes in the following manner:

$$5Na_2S_2O_7 \xrightarrow{TiO_2} 4Na_2S_2O_7 \cdot Na_2SO_4 + SO_3 \qquad (3)$$

The equation shows only the stoichiometry of the product formed, it should not infer that the product is just a double salt of sodium sulfate and pyrosulfate. The product should be a kind of polymer having the formula $Na_{10}S_9O_{32}$. The process is slightly exothermic with a DTA peak at 470°C for the 1 : 1 mole ratio. For the other mole ratios, the exothermic peak may not be seen because the process may be balanced thermally by a prior and post-endothermic change. The *d*-spacing values recorded for this reaction product are 9.43, 8.12, 6.88, 5.59, 4.86, 4.285, 3.99, 3.92, 3.708, 3.27, 3.07, 3.014, 2.88, 2.80, 2.717, 2.67 and 2.48 Å with the most intensive lines at 3.708, 3.92 and 6.88 Å. None of these lines correspond to sodium pyrosulfate or sodium sulfate. This compound could not be identified by referring to the A.S.T.M. cards.

The DTA curves show that a sharp and reproducible endothermic peak with a minimum point at 560°C characterizing the TiO_2–$Na_2S_2O_8$ mixtures at all mole ratios examined. By cooling the 1 : 1 molar mixture from 570°C to room temperature, it was observed that this endotherm corresponds to the melting of the reaction product. The white melt was leached with water and centrifuged. The insoluble fraction was dried and analyzed by X-ray diffraction and was found to consist entirely of TiO_2. Solid barium chloride particles were then added to the remaining solution and a white precipitate of barium sulfate was obtained. This indicates that the reaction product can be easily hydrolyzed with water to give the sodium sulfate.

The molten product undergoes immediate decomposition into sodium sulfate and a gaseous product which is mainly oxides of sulfur. The decomposition process was indicated by TG curves moving downward while the reaction product was indicated by the DTA melting endotherm at 880°C, which is the melting temperature of sodium sulfate.

It is worthwhile to point out that the final temperature and the rate of decomposition are affected by the amount of TiO_2 present. The final decomposition temperature was 960°C for the 1:2 mole ratio, 950°C for the 1:1, 915°C for the 2:1 and 750°C for the 4:1 (TiO_2–$Na_2S_2O_8$) mole ratio.

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