

Reactivity of Thermal Decomposition Products of Ammonium Metavanadate Towards Sodium Sulfite at Different Temperatures

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The present study is devoted to throw some light on the probable interactions between ammonium metavanadate and sodium sulfite which may help in preparation of vanadium-containing catalyst used in sulfuric acid industry. The probable interactions are in fact chemical reactions between the resulted reactive decomposition products of both salts. The reactive species produced from ammonium metavanadate are $(\text{NH}_4)_4\text{V}_6\text{O}_{17}\cdot 14\text{H}_2\text{O}$ and V_2O_5 whereas those produced from sodium sulfite are $\text{Na}_2\text{S}_5\text{O}_{16}$, Na_2O , Na_2SO_4 and Na_2S . The crystalline reaction products produced at different temperatures are $\text{Na}_2\text{V}_6\text{O}_{16}\cdot 3\text{H}_2\text{O}$, V_2S_3 , $\text{NaV}_6\text{O}_{15}$, NaV_3O_8 and $\text{Na}_8\text{V}_{24}\text{O}_{63}$. The factors which affect the formation and quantities of different products are discussed with the help of the results obtained from X-ray diffraction, electronic absorption spectra, thermogravimetric and chemicals analyses.

INTRODUCTION

The chemical reactions between ammonium metavanadate and different inorganic sulfur compounds were the subject of several studies¹⁻⁶ due to their importance in preparation of vanadium pentoxide catalyst which is used in several oxidation processes such as oxidation of sulfur dioxide in sulfuric acid industry.

The studies in the present article are considered as a continuation of the previous studies devoted to characterization of reaction products resulted from the interaction of ammonium metavanadate with KHSO_4 , NaHSO_4 , and NaHSO_3 . The study is devoted to investigate the probable reactions taking place between ammonium metavanadate and sodium sulfite with different molar ratios at different temperatures. The characterizations of reaction products were carried out using X-ray diffraction, electronic absorption spectra, thermal and chemical analyses.

EXPERIMENTAL

Chemicals: Sodium sulfite, ammonium metavanadate, potassium permanganate, ammonium ferrous sulfate and barium diphenylamine sulfonate indicator were obtained from BDH Company, England.

Reaction mixtures: Three reaction mixtures of ammonium metavanadate and sodium sulfite with molar ration 8 : 1 (I), 1 : 1 (II), and 1 : 2 (III) were prepared by mixing the starting chemicals followed by homogenizing and grinding. The sodium sulfite and the three mixtures were heated gradually ($10^\circ\text{C}/\text{min}$) in a static air from room temperature to the desired heating ones and kept constant for 4 h at that temperature. The heating temperatures are 250, 300, 400, 500, 600 and 700°C .

X-Ray diffraction patterns (XRD): The X-ray diffraction patterns of sodium sulfite before and after heating at different temperatures in addition to those of different reaction products were obtained at room temperature using a Philips diffractometer (type PW1051) employing Ni-filtered Co α 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 $2\theta \text{ min}^{-1}$.

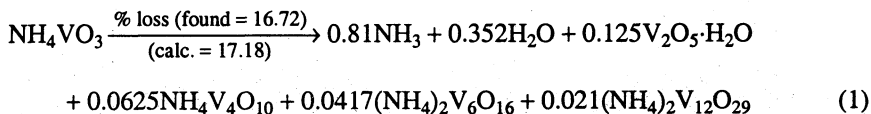
Thermal analysis: The thermogravimetric analyses of sodium sulfite and different reaction mixtures were carried out using Perkin-Elmer Delta Series (TGA 7) thermoanalyzer. The rate of heating, in the static air, was $10^\circ\text{C min}^{-1}$.

Chemical analysis: 0.5 g of each reaction mixture was ground and added to 50 mL water. The precipitate was rejected whereas the contents of the tri-, tetravalent vanadium species in the filtrate were determined according to the methods of analysis described elsewhere^{7, 10, 11}. The same procedure was repeated by extraction of different vanadium species in 0.5 M H_2SO_4 instead of water.

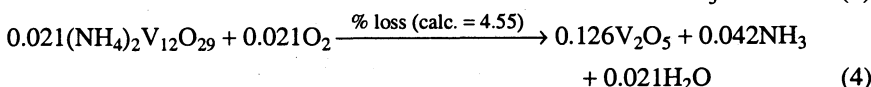
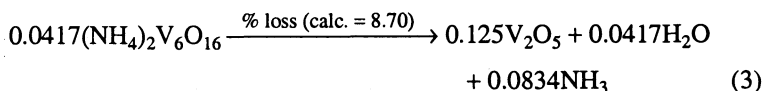
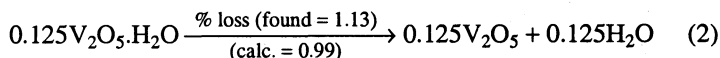
RESULTS AND DISCUSSION

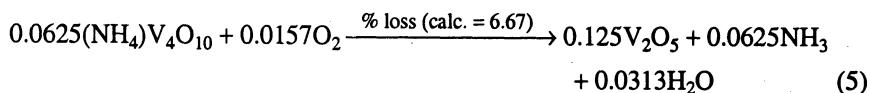
The characterization of the various reactive ingredients produced as a result of heating the two reactants (NH_4VO_3 and Na_2SO_3) individually at different temperatures is considered as a reasonable guide that helps in the investigation of the probable reaction which may have taken place between the two salts with different molar ratios at various temperatures.

The decomposition products of ammonium metavanadate⁷ were found to have started at 168–280°C leading to evolution of ammonia gas, water vapour, two ammonium bronzes ($\text{NH}_4\text{V}_4\text{O}_{10}$, $(\text{NH}_4)_2\text{V}_{12}\text{O}_{29}$), hydrated vanadium pentoxide ($\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$) and diammonium hexavanadate ($(\text{NH}_4)_2\text{V}_6\text{O}_{16}$). This decomposition step can be represented by the following equations,

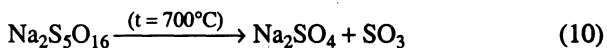
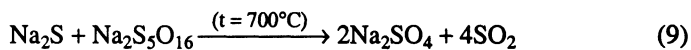
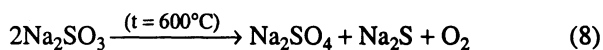
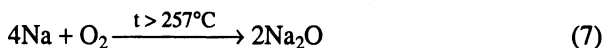
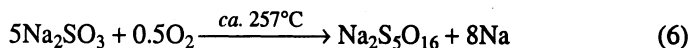


At 280–334°C the resulted hydrated vanadium pentoxide dehydrates to V_2O_5 , whereas diammonium hexavanadate dissociates to vanadium pentoxide, ammonia and water. At the same time the last three reaction products were also produced as a result of oxidation of the two ammonium bronzes by oxygen. These decomposition processes can be represented as follows:





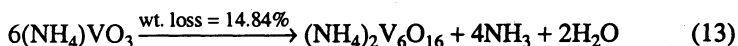
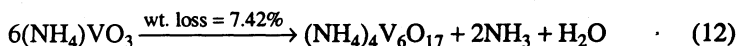
The second starting compound, Na_2SO_3 , was found to be oxidized to sodium sulfate¹² via formation of some intermediates such as $\text{Na}_2\text{S}_5\text{O}_{16}$ *, Na_2O and Na_2S . The different processes which lead to the transformation of sulfite to the corresponding sulfate can be represented by the following equations,



It is worthy to state that the probable reactions between the two salts are in fact reactions between the reactive products produced from their thermal decomposition products as can be seen later. The interaction between the two salts leads to lowering of their decomposition temperature which may be ascribed to the probable interaction (or coordination) between the nonbonding electrons of sulfite group and vanadium ion.

The thermogravimetric analysis of reaction mixtures I, II and III (Fig. 1) were carried out hoping to follow the successive reaction steps which were confirmed with the aid of the results obtained from X-ray diffraction patterns and electronic absorption spectra of solid reaction products and their acidic extract solutions respectively.

The first decomposition step of ammonium metavanadate, as appears from TG plots presented in Fig. 1, was found to be located at 167, 150 and 145°C for mixtures I, II, and III respectively. The percentages of weight losses estimated for the three mixtures amount to 11.68, 11.13 and 11.50% respectively and agree fairly with the theoretical value (11.13%) provided that ammonium metavanadate in the reaction mixture dissociates at lower temperatures compared to the pure salt and produce an equal mixture of the two polyvanadates $(\text{NH}_4)_4\text{V}_6\text{O}_{17} \cdot 14\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$. This assumption can be represented by the following equations:



*The sodium pentasulfate salt was firstly detected and reported elsewhere¹².

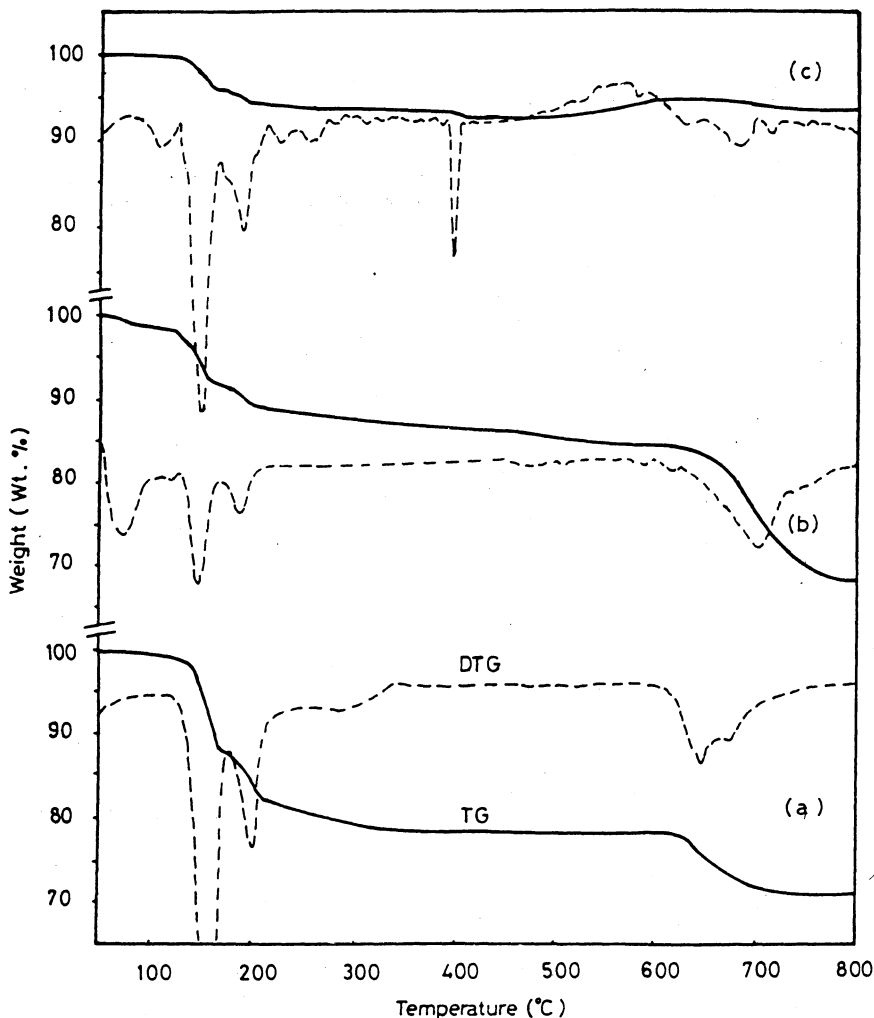


Fig. 1 TG and DTG traces of reaction mixture in air (heating rate = $10^{\circ}\text{C min}^{-1}$), mixture I (a), II (b) and III (c).

The presence of $(\text{NH}_4)_4\text{V}_6\text{O}_{17}\cdot 14\text{H}_2\text{O}$ was confirmed by the appearance of its characteristic X-ray diffraction patterns for decomposition products of different mixtures at 250°C (Table-1, Figs. 2–4) the production of tetraammonium polyvanadate from ammonium metavanadate gives an indication that the interaction of the last salt with sodium sulfite effects the pathway and identity of the products of decomposition, since it was found earlier that such compound is not produced in case of thermal decomposition of ammonium metavanadate alone⁷. The same compound $[(\text{NH}_4)_4\text{V}_6\text{O}_{17}\cdot 14\text{H}_2\text{O}]$ was investigated and indexed by Fedorov *et al.*¹³, and prepared later on by Andrukaitis *et al.*¹⁴ The disappearance of $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$, which was suggested to be produced according to eqn. (12), may

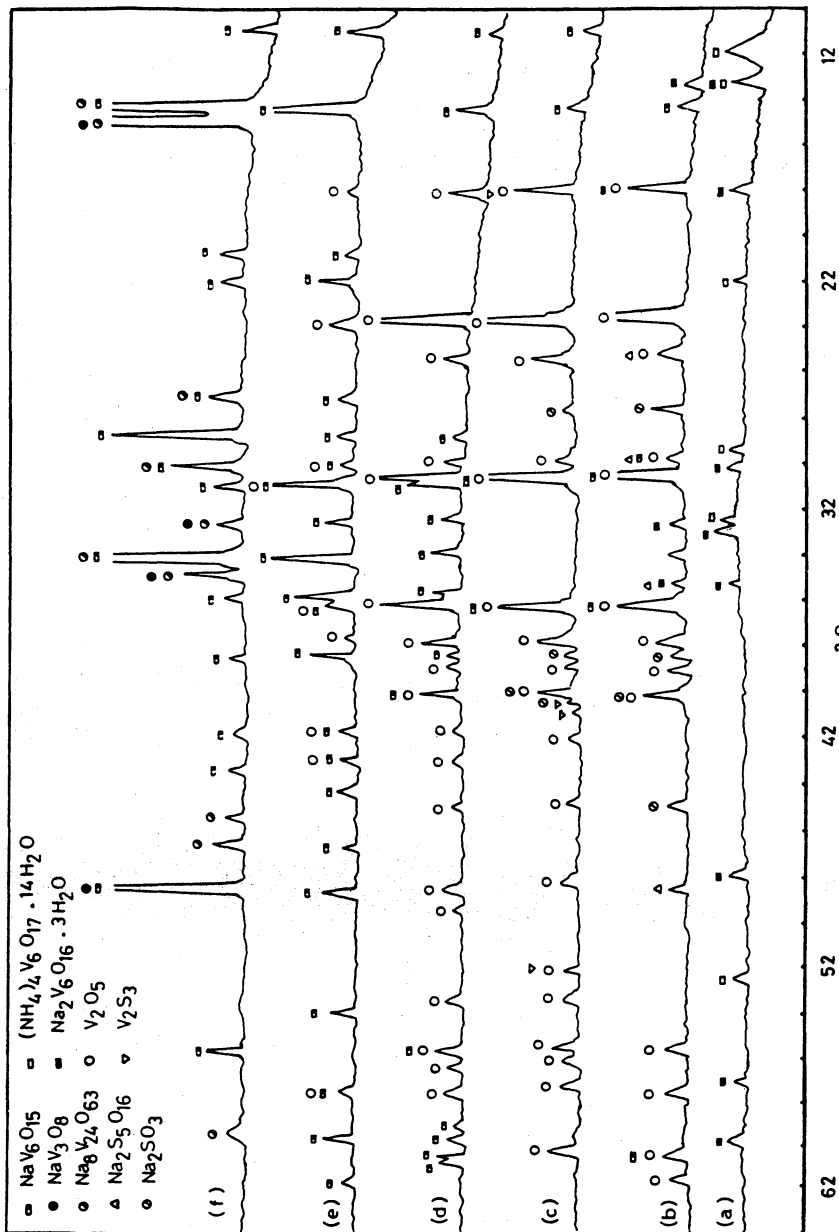


Fig. 2 X-ray diffraction patterns of reaction products mixture I heated for 4 h at 250 (a), 300 (b), 400 (c), 500 (d), 600 (e) and 700°C (f) using $\text{Co K}\alpha$ irradiation and iron filter.

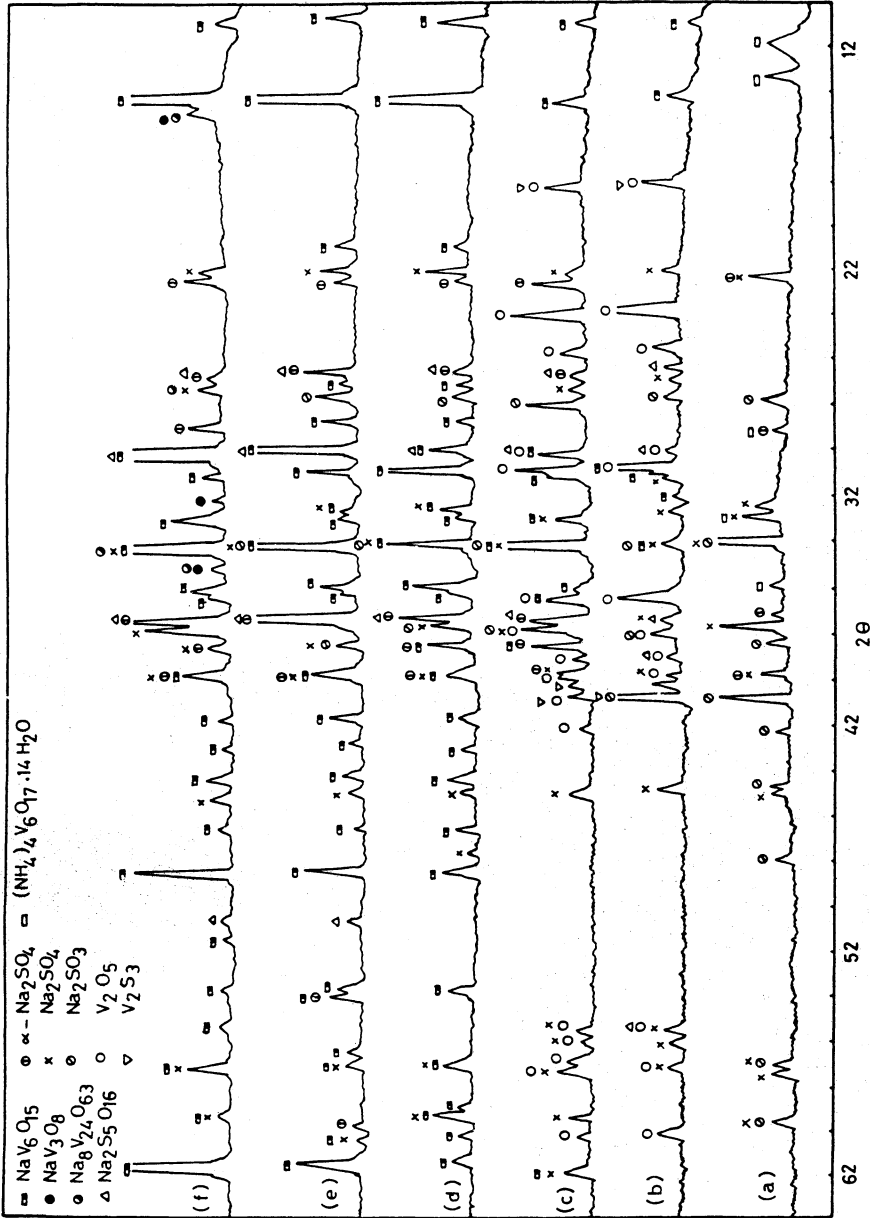


Fig. 3 X-ray diffraction patterns of reaction products mixture II heated for 4 h at 250 (a), 300 (b), 400 (c), 500 (d), 600 (e) and 700°C (f) using Co $K\alpha$ irradiation and iron filter.

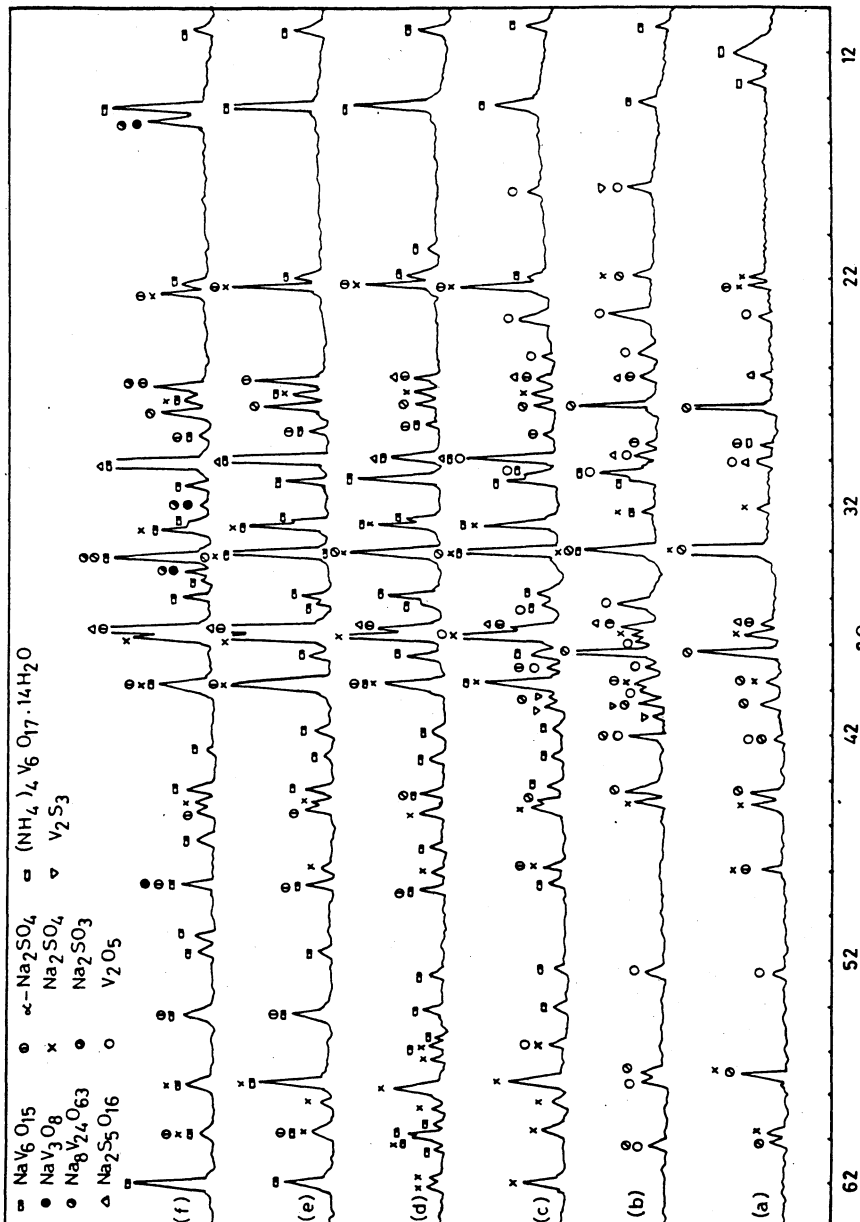
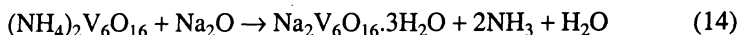


Fig. 4 X-ray diffraction patterns of reaction products mixture III heated for 4 h at 250 (a), 300 (b), 400 (c), 500 (d), 600 (e) and 700°C (f) using $\text{Co K}\alpha$ irradiation and iron filter.

TABLE-1
THE CRYSTALLINE PHASES DETECTED IN THE REACTION PRODUCTS FOR MIXTURES I, II, AND III AT DIFFERENT TEMPERATURES

Mixture	Temp. (°C)	Crystalline phases
8 : 1 (I)	250	(NH ₄)V ₆ O ₁₇ ·14H ₂ O, Na ₂ V ₆ O ₁₆ ·3H ₂ O
	300	V ₂ O ₅ , Na ₂ SO ₃ , NaV ₆ O ₁₅ , Na ₂ V ₆ O ₁₆ ·3H ₂ O, Na ₂ S ₅ O ₁₆
	400	V ₂ O ₅ , Na ₂ SO ₃ , NaV ₆ O ₁₅
	500	NaV ₆ O ₁₅ , V ₂ O ₅
	600	NaV ₆ O ₁₅ , V ₂ O ₅
	700	NaV ₆ O ₁₅ , NaV ₃ O ₈ , Na ₈ V ₂₄ O ₆₃
	1 : 1 (II)	250
300		V ₂ O ₅ , Vs ₂ S ₃ , Na ₂ SO ₃ , Na ₂ SO ₄ , α-Na ₂ SO ₄ , Na ₂ S ₅ O ₁₆
400		V ₂ O ₅ , Na ₂ SO ₄ , α-Na ₂ SO ₄ , V ₂ S ₃ , Na ₂ SO ₃ , Na ₂ S ₅ O ₁₆ , NaV ₆ O ₁₅
500		NaV ₆ O ₁₅ , Na ₂ SO ₄ , α-Na ₂ SO ₄ , Na ₂ SO ₃ , Na ₂ S ₅ O ₁₆
600		NaV ₆ O ₁₅ , Na ₂ SO ₄ , α-Na ₂ SO ₄ , Na ₂ SO ₃ , Na ₂ S ₅ O ₁₆
700		NaV ₆ O ₁₅ , α-Na ₂ SO ₄ , Na ₂ SO ₄ , NaV ₃ O ₈ , Na ₈ V ₂₄ O ₆₃ , Na ₂ S ₅ O ₁₆
1 : 2 (III)		250
	300	V ₂ O ₅ , Na ₂ SO ₄ , α-Na ₂ SO ₄ , Na ₂ SO ₃ , NaV ₆ O ₁₅ , Na ₂ S ₅ O ₁₆ , V ₂ S ₃
	400	Na ₂ SO ₄ , α-Na ₂ SO ₄ , NaV ₆ O ₁₅ , V ₂ O ₅ , Na ₂ SO ₃ , Na ₂ S ₅ O ₁₆ , V ₂ S ₃
	500	Na ₂ SO ₄ , α-Na ₂ SO ₄ , NaV ₆ O ₁₅ , Na ₂ SO ₃ , Na ₂ S ₅ O ₁₆
	600	NaV ₆ O ₁₅ , Na ₂ SO ₄ , α-Na ₂ SO ₄ , Na ₂ SO ₃ , Na ₂ S ₅ O ₁₆
	700	NaV ₆ O ₁₅ , Na ₂ SO ₄ , αNa ₂ SO ₄ , NaV ₃ O ₈ , Na ₂ SO ₃ , Na ₈ V ₂₄ O ₆₃ , Na ₂ S ₅ O ₁₆

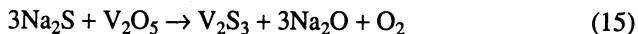
be ascribed to its reaction *in situ* with the active sodium oxide [produced from thermal oxidation of sodium sulfite, Eqn. (6)] leading to formation of Na₂V₆O₁₆·3H₂O according to the following equation:



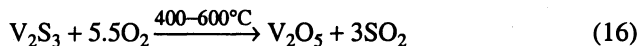
It seems that the degree of alkalinity of reaction products of mixture I is suitable for the formation of Na₂V₆O₁₆·3H₂O, since it is known that the last compound is prepared by slow evaporation of a solution of NaOH (0.22 M) and V₂O₅ (0.11 M) which adjusted to pH 3–6 by glacial acetic acid¹⁵. On the other hand it seems that the high degree of alkalinity of reaction products of mixtures II and III prevents the formation of Na₂V₆O₁₆·3H₂O due to the formation of excess amounts of sodium metal, Eqn. (6).

The appearance of sodium sulfate, which is the end product of thermal oxidation of sodium sulfite, at such low temperature (250°C) in the different reaction products may be ascribed to the presence of a reasonable coordination bonding between sulfite group and vanadium ions. This type of coordination or interaction may lead to conversion of sodium sulfite to different oxidation products such as Na₂S₅O₁₅, Na₂SO₄ and Na₂S at lower temperatures compared to that observed in case of the pure salt⁷. The formation of reducing sodium

sulfide, Eqn. (9), in a reactive form enhances its reaction with the reactive pentavalent vanadium species forming trivalent vanadium compound (V_2S_3). It is suggested that the (V_2S_3) compound was formed as a result of interaction between pentavalent vanadium compounds and sodium sulfide according to the following suggested equation:

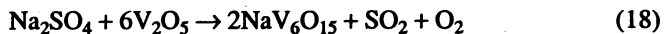
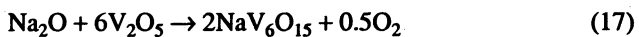


The species of V_2S_3 is known to be produced by the action of H_2S on V_2O_5 ^{16, 17}, where it is used as a catalyst for production of hydrogen from hydrogen sulfide¹⁸. An additional evidence for the presence of trivalent vanadium species was gained from the appearance of its characteristic electronic absorption spectra of solutions of reaction products, produced at 250, 300 and 400°C in 0.5 M H_2SO_4 (Table-2, Fig. 5). The appearance of electronic absorption bands characteristic for V^{4+} (Fig. 5) may be ascribed to the oxidation of a little amount of V_2S_3 to tetravalent species (not detected by X-ray diffraction patterns). This hypothesis was confirmed from the higher values of extraction of V^{3+} and V^{4+} compounds with 0.5 M H_2SO_4 compared to that determined for the extraction with water (Table-2). The species of trivalent and tetravalent vanadium compounds were found to be vanished completely at temperatures higher than 500°C due to their oxidation to pentavalent ones as can be seen from electronic absorption spectra and X-ray diffraction patterns (Table-1, Figs. 2–5). The oxidation of V_2S_3 to V_2O_5 , probably via formation of $VOSO_4$ ^{19, 20}, may be represented by the following equation:



The liberation of sulfur dioxide according to the previous equation may lead to the formation of sodium sulfite at such temperatures (400–600°C) as a result of reaction with sodium oxide produced from thermal oxidation of sodium sulfite. It is expected that a little part of sulfur dioxide may be oxidized to sulfur trioxide by the action of V_2O_5 which may act as an oxidizing catalyst. The liberation of a reducing sulfur dioxide gas led us to assume that the tetravalent vanadium compounds were formed with small quantities not sufficient enough to be detected by XRD but detected by electronic absorption spectra (Fig. 5) and estimated in the extraction solution of reaction products by water (Table-2).

It was found experimentally that the resulting active species of disodium hexavanadate which is formed by heating reaction mixture I at 250°C suffers from stability at higher temperatures and transformed to NaV_6O_{15} bronz²¹ (Table-1 and Fig. 2). The last bronz was also formed in the different reaction mixtures as a result of interaction between reactive sodium oxide (produced from thermal oxidation of sodium sulfite⁷) or sodium sulfate with the fresh vanadium pentoxide resulted from thermal decomposition of ammonium metavanadate⁷ according to the following equations^{22, 23}:



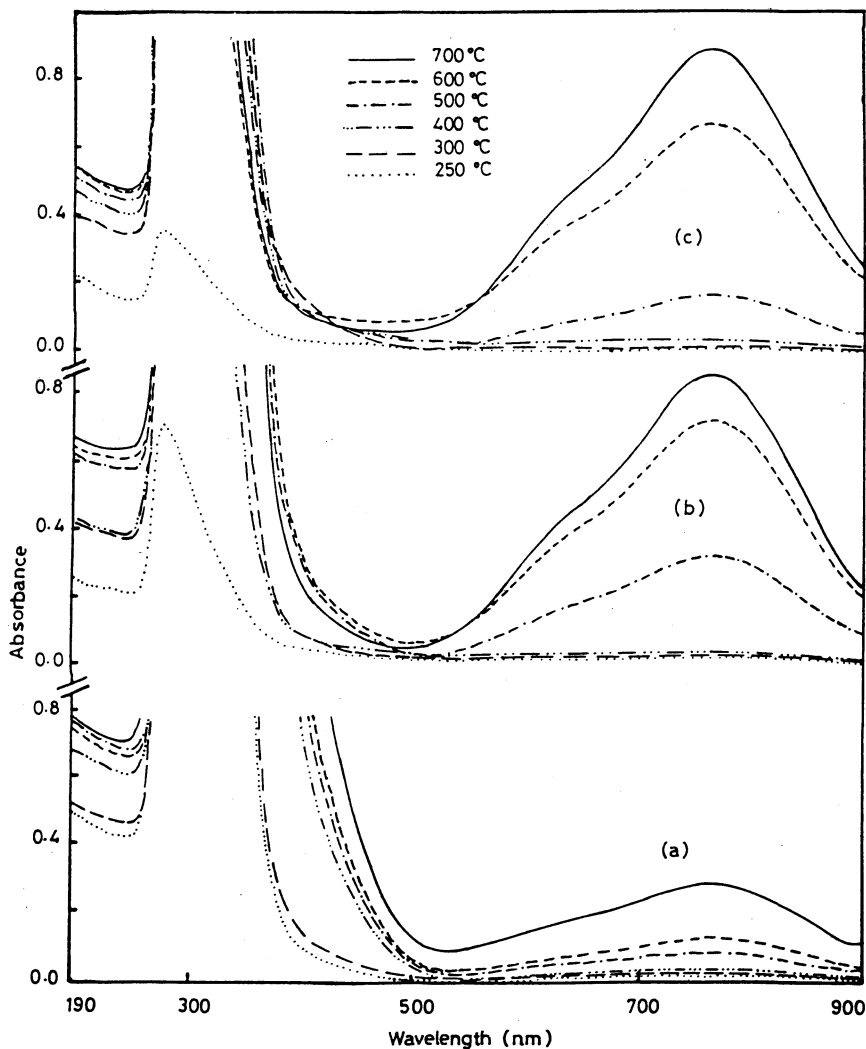


Fig. 5 Electronic absorption spectra of extract solution by 0.5 M M_2SO_4 of the reaction products of mixtures I (a), II (b) and III (c).

It was noticed experimentally that the disappearance of vanadium pentoxide above 600°C (Figs. 2–4) was associated with the formation of sodium trivanadate (NaV_3O_8) which transformed to $Na_8V_{24}O_{63}$ bronze^{21, 23, 24} according to equations (19) and (20).

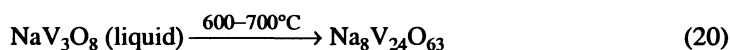


TABLE-2
EFFECT OF REACTION TEMPERATURE AND MOLAR RATIO BETWEEN NH_4VO_3
AND Na_2SO_3 ON THE EXTRACTION OF V_2O_5 BY 0.5 M H_2SO_4
AND WATER FROM REACTION PRODUCTS

Molar ratio between reactants	Temp. (°C)	Extraction by H_2SO_4		Extraction by water	
		% extn. V^{4+} (as V_2O_5)	% extn. V^{5+} (as V_2O_5)	% extn. V^{4+} (as V_2O_5)	% extn. V^{5+} (as V_2O_5)
8 : 1 (I)	250	4.32	35.26	0.88	0.59
	300	2.79	30.85	0.87	6.49
	400	2.08	29.87	0.84	6.14
	500	1.86	24.23	0.84	0.70
	600	1.48	11.33	0.64	0.90
	700	1.37	9.62	0.71	0.37
1 : 1 (II)	250	25.77	8.38	1.84	6.23
	300	22.67	10.74	1.82	16.28
	400	12.99	17.47	1.72	15.60
	500	1.81	2.41	1.72	2.33
	600	1.81	0.64	1.72	2.35
	700	1.62	1.96	1.60	2.51
1 : 2 (III)	250	24.20	6.92	1.94	8.80
	300	18.26	9.60	1.94	14.85
	400	5.63	17.19	1.94	7.12
	500	3.62	11.01	1.89	2.44
	600	0.84	0.51	1.96	0.82
	700	2.60	14.93	1.96	2.82

The appearance of $\text{Na}_8\text{V}_{24}\text{O}_{63}$ bronze in different reaction products at 600–700°C may be attributed to the liberation of acidic gases such as SO_2 and SO_3 , since it is known that the formation of polyvanadate anions is favoured at pH range between 2.20 and 7.25.

The variation of the values of weight losses of different reaction mixtures with increasing temperature of reaction above 250°C is considered as a resultant of weight losses due to reactions represented by eqns. (8)–(10), (12)–(15) and (17)–(20) and weight gained according to reactions represented by Eqns. (6), (7), and (16). So it is expected to notice an increase in the weight of reaction mixtures which contain higher amounts of sodium sulfite and lesser amounts of ammonium metavanadate as can be seen from Fig. 1.

It is worthy to mention that the percentages of extraction of vanadium from different reaction mixtures are considerably lower than those observed in case of reaction of ammonium metavanadate with KHSO_4^7 and NaHSO_4^8 . This phenomenon may be ascribed to the formation of more soluble vanadium compounds such as $\text{M}_2\text{VO}(\text{SO}_4)_2$ and $\text{M}_3\text{VO}_2(\text{SO}_4)_2$ where $\text{M} = \text{Na}$ or K . On the other hand the chemical reactions in the present study lead to the formation of less soluble compounds such as $\text{Na}_2\text{V}_6\text{O}_{16}$, V_2S_3 and different types of bronzes ($\text{NaV}_6\text{O}_{15}$, NaV_3O_8 and $\text{Na}_8\text{V}_{24}\text{O}_{63}$).

Conclusions

1. The identities of decomposition products of ammonium metavanadate in the present reaction mixtures differ significantly than those produced from heating the pure salt.
2. The decomposition temperatures of both ammonium metavanadate and sodium sulfite in their mixtures were found lower than those of the individual pure ones.
3. The chemical reaction of ammonium metavanadate with reducing sodium sulfite salt leads to production of high percentages of sodium bronzes (e.g., NaV_3O_8 , $\text{NaV}_6\text{O}_{15}$ and $\text{Na}_8\text{V}_{24}\text{O}_{63}$) and V_2S_3 in the reaction products whereas the reaction with NaHSO_4 and KHSO_4 leads to formation of high percentages of water-soluble tetra- and pentavalent vanadium compounds such as $\text{M}_2\text{VO}(\text{SO}_4)_2$ and $\text{M}_3\text{VO}_2(\text{SO}_4)_2$ where $\text{M} = \text{Na}$ or K .

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