

On the Reaction between Ammonium Metavanadate and Potassium Hydrogen Sulfate at Different Temperatures

M. F. R. Fouda,* H. I. Saleh,* W. H. Hegazy,† and E. A. Kishar‡

*Inorganic Chemistry Department, National Research Centre, Post Code No. 12622, 4 El-Tahrir Street, Dokki, Cairo, Egypt; †Faculty of Education, Suez Canal University, Suez, Egypt; and ‡Department of Chemistry, University College for Girls, Ain Shams University, Cairo, Egypt

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The reaction products resulting from the interaction of ammonium metavanadate and potassium hydrogen sulfate were characterized by chemical and thermal analysis, X-ray diffraction patterns, ligand field spectra, and magnetic susceptibility. The interaction between the two salts was found to start as early as 50°C. The identity of the products depends essentially on the temperature and time of reaction in addition to the molar ratio of the reactants. The product compounds were composed, in general, of bronzes and polyvanadates in addition to some tetra- and pentavalent vanadium compounds. The production of tetravalent vanadium compounds may arise via the intervention of diamagnetic dioxovanadium (V) sulfite $\text{VO}_2(\text{SO}_3)_{0.5}$ which is unstable above 200°C and transforms to vanadyl sulfate (VOSO_4) which in turn reacts with K_2SO_4 forming $\text{K}_2\text{VO}(\text{SO}_4)_2$. © 1999 Academic Press

INTRODUCTION

Investigations of reactions between pentavalent vanadium compounds such as ammonium metavanadate and various inorganic sulfur compounds are of great practical importance. This is because various vanadium compounds are used as catalysts for the complete combustion of hydrocarbons (1–3) and the oxidation of lower oxides, and some other substances, including carbon monoxide (4–6), nitrous oxide (7–9), ammonia (10–12), and sulfur dioxide (13–18) in the presence of air or oxygen. The oxidation of the first two gases is carried out by suitable methods to minimize pollution of the air, whereas the oxidations of the last two are used industrially, on a large scale, for production of nitric and sulfuric acids, respectively.

Despite the importance of studies of the reaction between ammonium metavanadate and potassium hydrogen sulfate at different temperatures, this has not been investigated and virtually nothing is known regarding the complex nature of such reactions. The present article constitutes the first part of a work on the chemistry of the catalytically and industrially important vanadium compounds produced as

a result of the interaction of ammonium metavanadate and some inorganic sulfur compounds. Keeping this in mind we aimed to achieve the proper reaction conditions suitable for the production of an active catalyst used in the oxidation of sulfur dioxide. In addition, identification of the occurrence of chemical reactions between the two compounds may throw some light on the process of the extraction of vanadium by KHSO_4 from boiler fly ash.

EXPERIMENTAL

Chemicals

The starting materials, potassium hydrogen sulfate (KHSO_4), ammonium metavanadate (NH_4VO_3), and chemicals used in determination of tetra- and pentavalent vanadium (e.g., KMnO_4 , $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ and barium diphenylamine-sulfonate indicator) were provided by B.D.H. Chemicals Company, England.

Preparation of Reaction Mixtures

Three reaction mixtures composed of ammonium metavanadate and potassium hydrogen sulfate with molar ratios 8:1(I), 1:1(II), and 1:2(III) were prepared by mixing the solid reactants, homogenizing, and grinding. This process was followed by sieving below 200 mesh (particle size under 75 μm). Pure potassium hydrogen sulfate and the three mixtures were heated gradually (10°C/min) from ambient to reaction temperature and maintained constant at 50, 100, 250, 300, 400, 500, 600, or 700°C for 4 hours.

Chemical Analysis

The preparation of extract solutions containing the reaction products and the methods of determining of the vanadium species (V^{4+} , V^{5+}) therein were as described previously (19, 20).

Techniques and Measurements

The thermal analysis by TG and DTG of potassium hydrogen sulfate and ammonium metavanadate used a Delta series DTG A7 thermoanalyzer (USA) with a differential scanning calorimeter cell. The rate of heating was 10°C/min in a stream of air at 30 cm³/min.

X-ray power diffraction patterns of chilled samples of the heated products were obtained using a Philips diffractometer (type PW1051) employing either Fe-filtered CoK α or Ni-filtered CuK α radiation. The diffraction angle (2θ) was scanned at a rate of 2° min⁻¹.

The ligand-field spectra of the extract solutions, obtained by digestion of 0.25 g of reaction products with 100 ml of water for 15 min, were measured with a Shimadzu UV-240 automatic spectrometer (Japan).

The mass magnetic susceptibility, X_g in c.g.s. units, was measured using a Sherwood Scientific Ltd. magnetic susceptibility balance (England).

RESULTS AND DISCUSSION

Although the thermal decomposition of NH₄VO₃ has been studied by many investigators (18, 21–23), the mechanism of the decomposition reaction and the oxidation number of the resulting vanadium compounds are, still, the subject of controversy. The differences in the composition of the decomposition products, in the various studies, may be ascribed to variations in the experimental conditions including heating in a stream of oxidizing, reducing, inert gases or in vacuum. This might account for the contradictory results obtained by the different investigators. The present study aimed to investigate thoroughly the reactive species produced which may interact with those resulting from potassium hydrogen sulfate heated at different temperatures.

The X-ray diffraction patterns (Fig. 1) of ammonium metavanadate heated to 240°C at 10°C/min show that the decomposition products were composed of NH₄VO₃ (unchanged), (NH₄)₂V₆O₁₆, V₂O₅·H₂O, in addition to the two bronzes (NH₄)₂V₁₂O₂₉ and (NH₄)₂V₁₂O₂₉). The presence of the last two bronzes was confirmed by a slightly positive value of the magnetic moment. The existence of the (NH₄)₂V₁₂O₂₉ phase has also been observed by Joseph *et al.* (24). Based on the weight loss due to the evolution of ammonia gas and water vapor, and phases characterized by XRD identified by data on ASTM cards, the first decomposition step of ammonium metavanadate (168–280°C) can be represented by

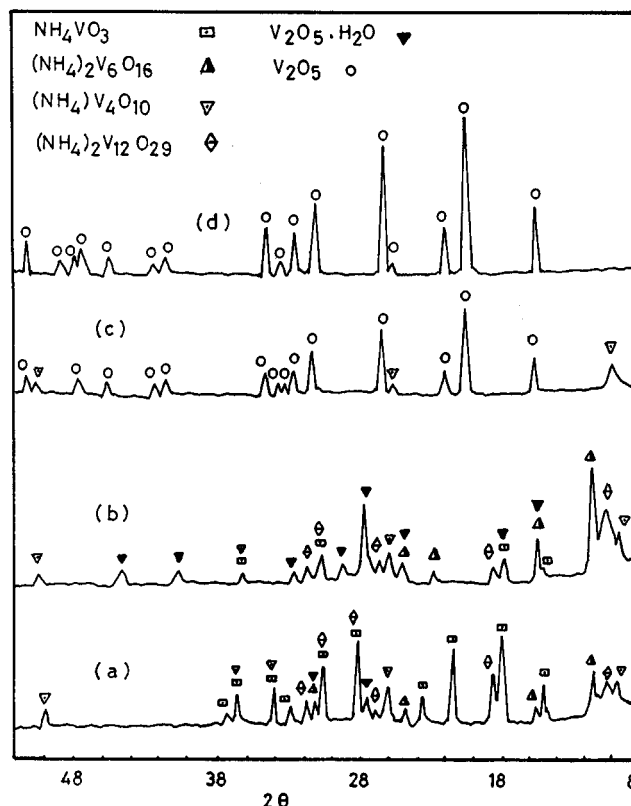
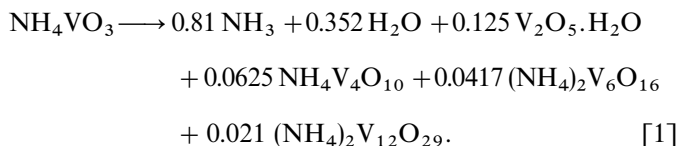
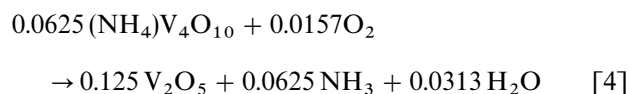
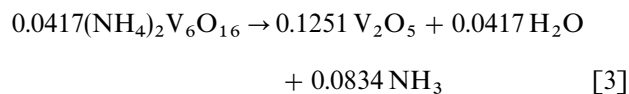
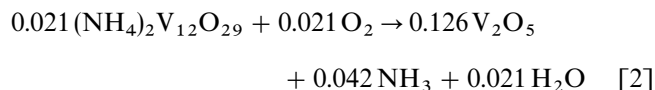


FIG. 1. X-ray diffraction patterns of decomposition products of NH₄VO₃ heated for 4 hours at 200 (a), 240 (b), 320 (c), and 420°C (d) using CuK α radiation and a nickel filter.

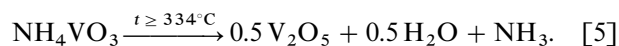
The measured weight loss (16.72%) is in fair agreement with that calculated (17.18%). The chemical analysis of ammonium metavanadate heated at 10°C/min to 280°C and quenched to room temperature, showed that the V⁵⁺/V⁴⁺ ratio was 6:1 in accordance with Eq. [1].

The second step, occurring between 280–334°C, corresponds to dehydration of the constituent (0.125 V₂O₅·H₂O); measured weight loss was 1.13% compared with 0.99% (expected value).

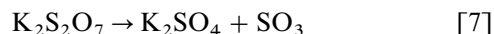
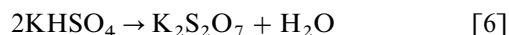
The third decomposition between 334 and 375°C was consistent with the following reactions:



The overall calculated loss in Eqs. [2]–[4] was 6.64% $\{=(4.55 + 8.70 + 6.67)/3\}$ which is in reasonable agreement with that measured (6.15%). The diamagnetic properties of the reaction product were confirmed from the measurement of its magnetic moment. This means that the vanadium oxide produced was not involved in any oxidation process of ammonia. Overall these reactions can be summarized by



On heating, KHSO_4 is transformed into water vapor and potassium pyrosulfate gradually between 220–405°C, yielding potassium sulfate (25) and sulfur trioxide above 640°C, probably via two intermediates at 638 and 693°C as appeared from the results of thermogravimetric analysis.



X-ray diffraction patterns of products produced at 535°C showed that these were a mixture of K_2SO_4 (vii) and $\text{K}_2\text{S}_2\text{O}_7$ (viii). The pyrosulfate is thermally unstable above 395°C and transforms to compound (vii).

INVESTIGATION OF THE REACTION BETWEEN AMMONIUM METAVANADATE AND POTASSIUM HYDROGEN SULFATE AT VARIOUS TEMPERATURES

The products formed as a result of reactions between KHSO_4 and NH_4VO_3 (in molar ratios, 8:1 (I), 1:1 (II), and 1:2 (III)) at temperatures 50, 100, 250, 300, 400, 500, 600, and 700°C were characterized by means of chemical analysis, electronic absorption spectra, magnetic susceptibility, and X-ray diffraction patterns. The reaction products were generally composed of the following compounds: $(\text{NH}_4)_2\text{V}_{12}\text{O}_{29}$ (24) (i), V_2O_5 (ii), $\text{K}_2\text{V}_8\text{O}_{21}$ (26–28) (iii), $\text{K}_{0.33}\text{V}_2\text{O}_5$ (29) (iv), KV_6O_{15} (30) (v), KV_3O_8 (31, 32) (vi), K_2SO_4 (vii), $\text{K}_2\text{S}_2\text{O}_7$ (viii), KVO_2SO_4 (33–35) (ix), $\text{K}_3\text{VO}_2(\text{SO}_4)_2$ (35) (x), $\text{K}_4(\text{VO}_2)_2(\text{SO}_4)_2\text{S}_2\text{O}_7$ (33–35) (xi), $\text{VO}_2(\text{SO}_3)_{0.5}$ (36) (xii), $(\text{VO}_2)_2\text{S}_2\text{O}_7$ (37) (xiii), VOSO_4 (38–40) (xiv), and $\text{K}_2\text{VO}(\text{SO}_4)_2$ (40) (xv) (Table 1).

a. Mixture III

The reaction products depend on both temperature and reactant composition. After heating mixture III at 50°C (Fig. 2) six crystalline compounds (vii, viii, ix, x, xi, and xv) were identified in the products; the first two were produced

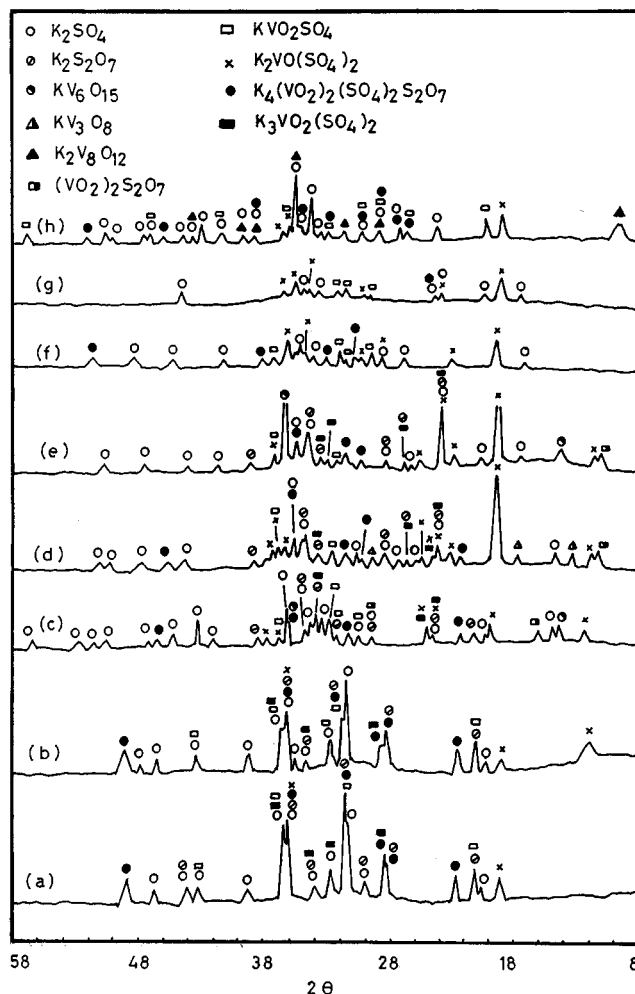
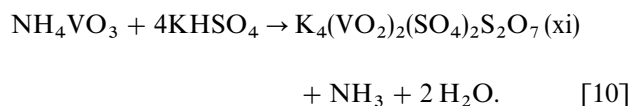
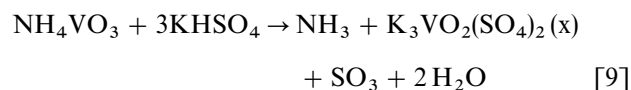
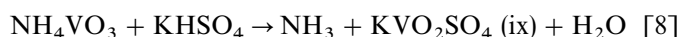


FIG. 2. X-ray diffraction patterns of reaction products produced from an interaction between NH_4VO_3 and KHSO_4 (mixture III) heated for 4 hours at 50 (a), 100 (b), 250 (c), 300 (d), 400 (e), 500 (f), 600 (g), and 700°C (h) using $\text{CoK}\alpha$ radiation and an iron filter.

according to Eqs. [6] and [7], and others by



It seems that (xv) (Fig. 2) was produced by the interaction of potassium hydrogen sulfate with a tetravalent vanadium intermediate such as VOSO_4 . This is a possible thermal

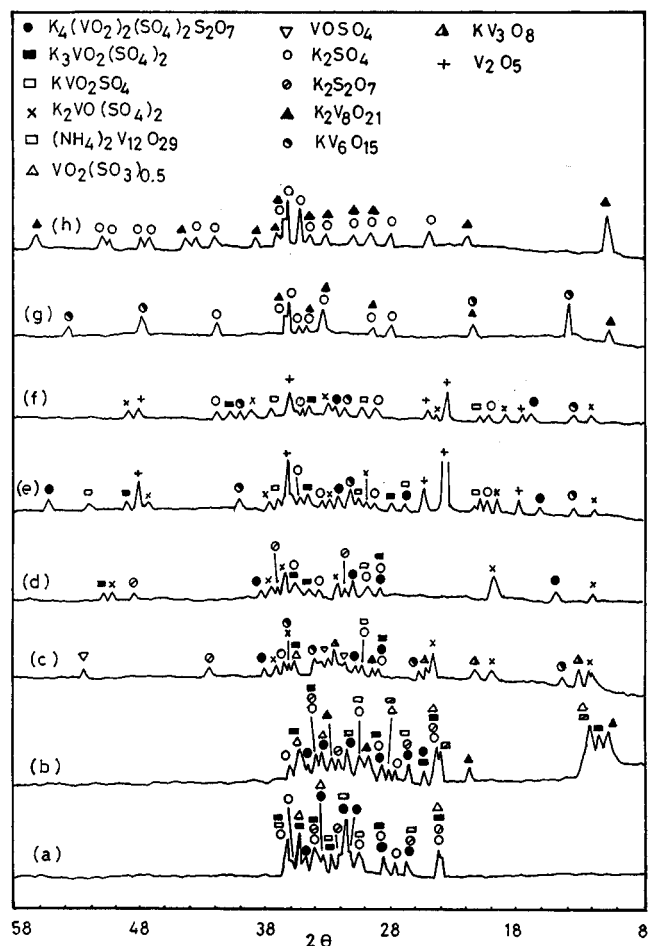
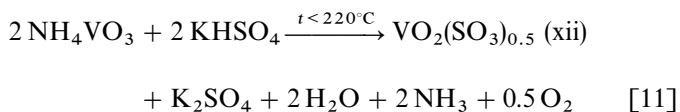
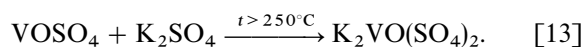
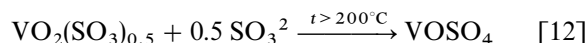


FIG. 3. X-ray diffraction patterns of reaction products produced from interaction between NH_4VO_3 and KHSO_4 (mixture II) heated for 4 hours at 50 (a), 100 (b), 250 (c), 300 (d), 400 (e), 500 (f), 600 (g), and 700°C (h) using $\text{CoK}\alpha$ radiation and an iron filter.

decomposition product of compound $\text{VO}_2(\text{SO}_3)_{0.5}$ (xii)¹ and may be formed at a relatively low temperature ($t \leq 200^\circ\text{C}$) (3) but is decomposed at higher temperatures. Therefore its characteristic diffraction patterns were observed in mixture II at 50–250°C (Fig. 3), but not in mixture III. This may be due to the evolution of a relatively large quantity of heat in the last mixture leading to its transformation directly to tetravalent vanadium compound $\text{K}_2\text{VO}(\text{SO}_4)_2$ (xv). The formation of compounds (xii), (xiv), and (xv) may be represented as follows:

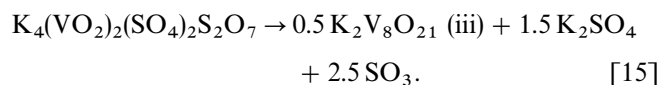
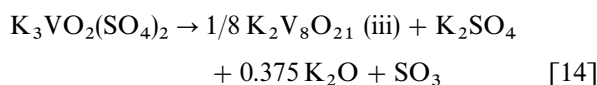


¹The measurements of magnetic susceptibility of reaction products of mixture II, which was heated at 50 and 100°C, indicated that the products are diamagnetic. This means that the value of x in the compound $\text{VO}_2(\text{SO}_3)_x$ (36) equals 0.5.



The conversion of vanadyl sulfate (xiv) into potassium oxovanadium (IV) sulfate (xv) was confirmed by the disappearance of characteristic diffraction patterns of VOSO_4 and a large increase of the intensity of X-ray diffraction patterns of $\text{K}_2\text{VO}(\text{SO}_4)_2$ shown in Fig. 2.

On raising the reaction temperature for mixture III above 300°C, it seems (according to Fig. 2) that both compounds $\text{K}_3\text{VO}_2(\text{SO}_4)_2$ and $\text{K}_4(\text{VO}_2)_2(\text{SO}_4)_2\text{S}_2\text{O}_7$ were transformed³ to potassium octavanadate (V) ($\text{K}_2\text{V}_8\text{O}_{21}$) and potassium sulfate as follows:

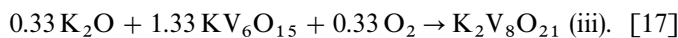


This hypothesis was confirmed from the practical finding which shows a gradual increase in the peak height of the X-ray diffraction patterns of potassium sulfate on increasing the reaction temperature to 700°C. $\text{K}_3\text{VO}_2(\text{SO}_4)_2$ (x) was noted to decompose completely at temperatures higher than 400°C (35) and transform to compound (iii), whereas $\text{K}_4(\text{VO}_2)_2(\text{SO}_4)_2\text{S}_2\text{O}_7$ (35) (xi) shows a smaller tendency toward transformation to compound (iii) compared with compound (x), as can be seen from its existence even at 700°C.

Furthermore, $\text{K}_2\text{VO}(\text{SO}_4)_2$ was oxidized to (KVO_2SO_4) above 300°C as shown by the gradual increase of peak of compound (ix) accompanied by a decrease of the peak of compound (xv) (Fig. 2) represented by



The reactive potassium oxide species seems to react instantaneously with KV_6O_{15} bronze yielding $\text{K}_2\text{V}_8\text{O}_{21}$:



The X-ray diffraction patterns at 700°C confirmed that the reaction products were predominantly K_2SO_4 ,

²The species of sulfur trioxide gas was liberated from decomposition of $\text{K}_2\text{S}_2\text{O}_7$.

³The liberation of sulfur trioxide from compound (xi) which heated at ca. 400°C was also observed by M. P. Glazyrin *et al.*, who prepared and characterize a series of oxosulfatovanadates of alkaline earth metals (33, 35). On the other hand, the effect of temperature on compound (x) was not explained clearly by them (35).

$\text{KVO}_2(\text{SO}_4)$, and $\text{K}_2\text{V}_8\text{O}_{21}$ with small amounts of the less stable $\text{K}_4(\text{VO}_2)_2(\text{SO}_4)_2(\text{S}_2\text{O}_7)$ and $\text{K}_2\text{VO}(\text{SO}_4)_2$.

b. Mixture II

The reaction products at 50 and 100°C from mixture II resemble those from mixture III, except for the formation of $\text{VO}_2(\text{SO}_3)_{0.5}$ identified by X-ray diffraction (Fig. 3). This difference is ascribed to the exothermic character of reactions [8–10] but the quantity of heat evolve here was not sufficient to decompose $\text{VO}_2(\text{SO}_3)_{0.5}$ (xii) which, usually, decomposes to VOSO_4 which is transformed to $\text{K}_2\text{VO}(\text{SO}_4)_2$ as in mixture III (Table 1, Figs. 2, 3, and Eqs. [12], [13]).

At 250°C or above the quantity of sulfate and/or pyrosulfate present is apparently insufficient to transform all vanadium species into compounds which possess a high potassium:vanadium ratio such as KVO_2SO_4 , $\text{K}_3\text{VO}_2(\text{SO}_4)_2$, and $\text{K}_4(\text{VO}_2)_2(\text{SO}_4)_2\text{S}_2\text{O}_7$. This situation also leads to the formation of potassium triivanadate (KV_3O_8) and potassium octavanadate ($\text{K}_2\text{V}_8\text{O}_{21}$), in addition to KV_6O_{15} bronze which is characterized by a low ratio of K:V. The disappearance of KV_6O_{15} bronze at 700°C may be explained as before in mixture III. The absence of dioxovanadium pyrosulfate ($\text{VO}_2)_2\text{S}_2\text{O}_7$ (xiii) in the reaction product of such a mixture may be ascribed to a deficiency of acidic species such as sulfate and pyrosulfate (41, 42).

TABLE 1
The Crystalline Phases Detected in Reaction Products for Mixtures I, II, and III at Different Temperatures

| Molar ratio $\text{NH}_4\text{VO}_3:\text{KHSO}_4$ | Temp. (°C) | Crystalline phases |
|---|------------|---|
| 8:1 (I) | 50 | NH_4VO_3 |
| | 100 | NH_4VO_3 , i |
| | 250 | i |
| | 300–400 | ii |
| | 500–600 | ii, iii |
| | 700 | ii, iii, iv |
| 1:1 (II) | 50 | vii, viii, ix, x, xi, xii |
| | 100 | i, iii, vii, viii, ix, x, xi, xii |
| | 250 | v, vi, vii, viii, ix, x, xi, xii, xiv, xv |
| | 300 | vii, viii, ix, x, xi, xv |
| | 400–500 | ii, v, vii, ix, x, xi, xv |
| | 600 | iii, v, vii |
| | 700 | iii, vii |
| 1:2 (III) | 50–100 | vii, viii, ix, x, xi, xv |
| | 250 | v, vii, viii, ix, x, xi, xiii, xv |
| | 300 | vi, vii, viii, ix, x, xi, xiii, xv |
| | 400 | v, vii, viii, ix, x, xi, xiii, xv |
| | 500–600 | vii, ix, xi, xv |
| | 700 | iii, vii, ix, xi, xv |

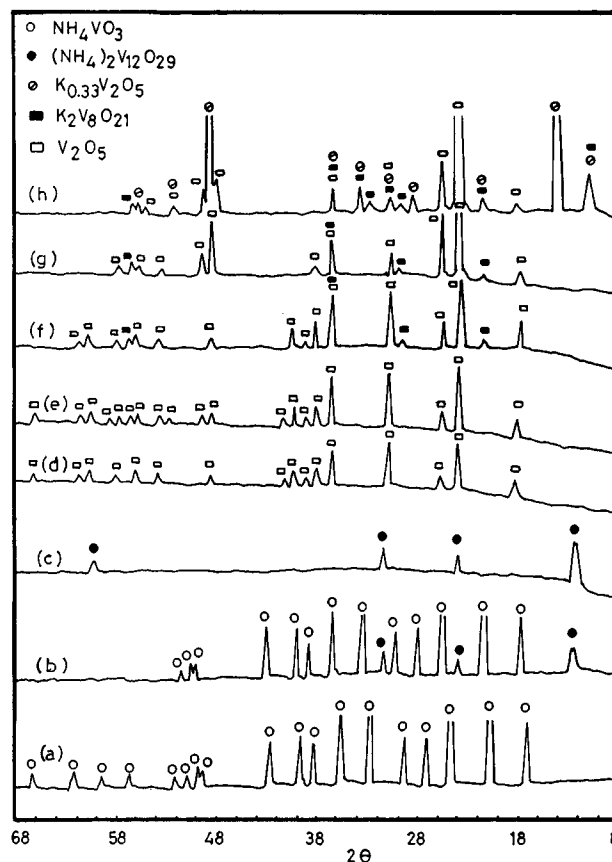


FIG. 4. X-ray diffraction patterns of reaction products produced from interaction between NH_4VO_3 and KHSO_4 (mixture I) heated for 4 hours at 50 (a), 100 (b), 250 (c), 300 (d), 400 (e), 500 (f), 600 (g), and 700°C (h) using $\text{CoK}\alpha$ radiation and an iron filter.

c. Mixture I

The reaction products obtained on heating mixture I (Fig. 4 and Table 1) differ from those produced from the other two mixtures. This may be because the quantity of potassium present in K_2SO_4 and/or $\text{K}_2\text{S}_2\text{O}_7$ is insufficient to produce compounds with high K:V ratios such as $\text{KVO}_2(\text{SO}_4)$, $\text{K}_3\text{VO}_2(\text{SO}_4)_2$, $\text{K}_4(\text{VO}_2)_2(\text{SO}_4)_2\text{S}_2\text{O}_7$, and $\text{K}_2\text{VO}(\text{SO}_4)_2$ in significant quantities. The presence of soluble pentavalent and tetravalent species such as $\text{K}_2\text{VO}(\text{SO}_4)_2$ was detected spectroscopically (see below). This was confirmed in the eluates obtained from different reactions (Table 2). This also explains the appearance of unreacted ammonium metavanadate and some of its decomposition products.

EXTRACTION OF VANADIUM FROM THE NH_4VO_3 - KHSO_4 REACTION PRODUCTS AT DIFFERENT TEMPERATURES

The extraction of vanadium oxide (as soluble salts by cold water) from the reaction products of mixtures I–III after

TABLE 2
Effect of Reaction Temperature and Molar Ratio between Reactants on the Percentage of Extraction of V₂O₅ from Different Reaction Products by Cold and Boiling Water

| Molar ratio NH ₄ VO ₃ :KHSO ₄ | Temp. (°C) | % extn. of V ₂ O ₅ (as V ⁴⁺) | | % extn. of V ₂ O ₅ (as V ⁵⁺) | |
|---|------------|--|---------------|--|---------------|
| | | Cold water | Boiling water | Cold water | Boiling water |
| 8:1 (I) | 50 | | 0.62 | | 38.56 |
| | 100 | | 0.61 | | 38.33 |
| | 250 | 1.0 | 1.94 | 0.5 | 33.35 |
| | 300 | 5.0 | 2.62 | 0.5 | 36.43 |
| | 400 | | 0.95 | | 36.44 |
| | 500 | 1.0 | 0.96 | 5.5 | 36.96 |
| | 600 | | 0.87 | | 33.86 |
| | 700 | 0.5 | 1.29 | 3.3 | 37.84 |
| 1:1 (II) | 50 | | 1.22 | | 34.32 |
| | 100 | | 1.2 | | 35.27 |
| | 250 | 4.6 | 2.54 | 6.0 | 20.18 |
| | 300 | 47.0 | 11.69 | 4.0 | 18.7 |
| | 400 | | 5.81 | | 25.55 |
| | 500 | 12.0 | 4.41 | 37.0 | 27.96 |
| | 600 | | 5.88 | | 30.16 |
| | 700 | 1.0 | 1.94 | 10.0 | 38.79 |
| 1:2 (III) | 50 | | 1.55 | | 36.21 |
| | 100 | | 1.51 | | 31.91 |
| | 250 | 12.0 | 5.03 | 47.0 | 29.65 |
| | 300 | 88.0 | 21.0 | 9.0 | 3.96 |
| | 400 | | 14.82 | | 9.41 |
| | 500 | 38.0 | 9.46 | 46.0 | 19.65 |
| | 600 | | 9.03 | | 20.14 |
| | 700 | 2.0 | 2.56 | 28.0 | 39.74 |

heating 4 hours at 50–700°C increases with increasing the molar ratios between reactants heated as can be seen from results presented in Table 2.

The highest percentage of extraction of tetravalent vanadium species was attained following reactions at 300°C (Table 2). This finding may be attributed to the transformation of VO₂(SO₃)_{0.5} to VO SO₄ and K₂VO(SO₄)₂ above 250°C (Eqs. [12], [13]). On raising the temperature of reaction to 300°C or above the tetravalent species is transformed to the pentavalent state (KVO₂SO₄) by oxidation (Eq. [16]). This change leads to a decrease in the percentage extraction of tetravalent species which is associated with an increase in the pentavalent species (Table 2). Above 500°C the extraction percentages of both tetra- and pentavalent species were found to decrease due to transformation of pentavalent compounds into the less soluble polyvanadates (Eqs. [14], [15]). The presence of tetravalent species was also confirmed by the spectra of the extract solutions (two absorption bands at 760 and at 625 nm as a shoulder), as observed for the spectra of VO⁺⁺ in 0.5 to 2 M HClO₄ (43–45). The electronic transitions for two such peaks can be assigned for ²Γ₁₃ to ²Γ₁₄ and ²Γ₁₃ to ²Γ₁₁, respectively (43), provided that the hexaaquo-oxovanadium (IV) ions possess

a tetragonally distorted symmetry. The peak heights of the spectra of the extract solutions was found to increase gradually on raising the heating temperature reaching a maximum at 300°C, after which it decreases at higher reaction temperatures as shown in Fig. 5.

The values of extraction of tetravalent compounds by boiling water are low compared with those resulting from extraction with cold water (Table 2). This finding may be attributed to hydrolysis and the formation of insoluble VO(OH)₂ (46). On the other hand the increased extraction of pentavalent species may be considered to result from a rise in solubility with increasing temperature (47) and its decrease due to transformation of VO₂(SO₃)_{0.5} to insoluble VO(OH)₂ (probably via VOSO₄) by boiling water.

CONCLUSIONS

1. Ammonium metavanadate was found to react with potassium hydrogen sulfate as early as 50°C. These lead reactions to the formation of a variety of pentavalent vanadium compounds in addition to the tetravalent state that appeared in mixtures rich with potassium hydrogen sulfate. The identity and relative abundance of these

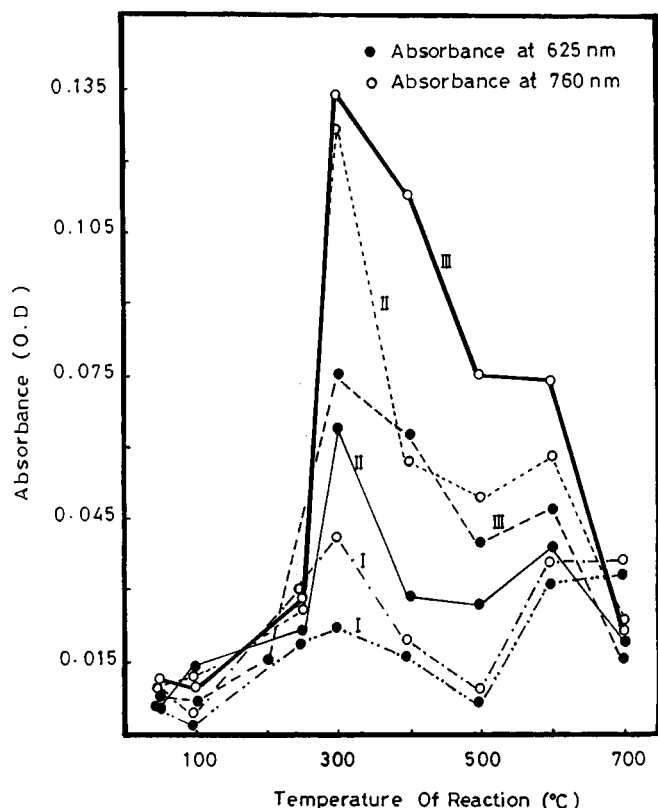


FIG. 5. Variation of the absorption at 625 and 760 nm of the extract solutions of reaction products produced by heating mixtures I, II, and III at different temperatures.

products depends on the molar ratio and temperature of reaction.

2. The dioxovanadium sulfite ($\text{VO}_2(\text{SO}_3)_{0.5}$) which is formed at 50°C is thermally unstable and transforms to $\text{K}_2\text{VO}(\text{SO}_4)_2$ via formation of VOSO_4 on heating above 250°C . The former compound was found to oxidize to $\text{KVO}(\text{SO}_4)_2$ above 300°C .

3. The two dioxovanadium sulfates ($\text{K}_3\text{VO}_2(\text{SO}_4)_2$ and $\text{K}_4(\text{VO}_2)_2(\text{SO}_4)_2\text{S}_2\text{O}_7$) formed below 200°C are thermally unstable above 250°C and transform to potassium octavanadate ($\text{K}_2\text{V}_8\text{O}_{21}$), whereas $\text{KVO}(\text{SO}_4)_2$ was found to be stable up to 700°C .

4. An increase in the molar ratio of potassium hydrogen sulfate with respect to ammonium metavanadate in reaction mixtures leads to a significant increase of water soluble tetra- and pentavalent vanadium compounds in reaction products. The solubilization of reaction products in boiling water increases the rate of hydrolysis of tetravalent species and the formation of insoluble hydrated $\text{VO}(\text{OH})_2$, and so leads to a decrease in the percentage of extraction of different vanadium species compared to extraction by cold water.

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