



# Evidence of quasi-intramolecular redox reactions during thermal decomposition of ammonium hydroxodisulfiteferrate(III), $(\text{NH}_4)_2[\text{Fe}(\text{OH})(\text{SO}_3)_2]\cdot\text{H}_2\text{O}$

Tünde Kocsis<sup>1</sup> · József Magyar<sup>2</sup> · István E. Sajó<sup>3</sup> · Tibor Pasinszki<sup>4</sup> · Zoltán Homonnay<sup>4</sup> · Imre M. Szilágyi<sup>5</sup> · Attila Farkas<sup>6</sup> · Zoltán May<sup>1</sup> · Herta Effenberger<sup>7</sup> · Sándor Szakáll<sup>8</sup> · Rajendra P. Pawar<sup>9</sup> · László Kótai<sup>1</sup>

Received: 5 October 2017 / Accepted: 3 December 2017 / Published online: 11 December 2017

© Akadémiai Kiadó, Budapest, Hungary 2017

## Abstract

Synthesis of ammonium hydroxodisulfiteferrate(III), (diammonium *catena*-{bis( $\mu^2$ -sulfito- $\kappa\text{O},\kappa\text{O}$ )- $\mu^2$ -hydroxo- $\kappa^2\text{O}$ }ferrate(III) monohydrate)  $(\text{NH}_4)_2[\text{Fe}(\text{OH})(\text{SO}_3)_2]\cdot\text{H}_2\text{O}$  (compound **1**) and its thermal behavior is reported. The compound is stable in air. Its thermal decomposition proceeds without the expected quasi-intramolecular oxidation of sulfite ion with ferric ions. The disproportionation reaction of the ammonium sulfite, formed from the evolved  $\text{NH}_3$ ,  $\text{SO}_2$  and  $\text{H}_2\text{O}$  in the main decomposition stage of **1**, results in the formation of ammonium sulfate and ammonium sulfide. The ammonium sulfide is unstable at the decomposition temperature of **1** (150 °C) and transforms into  $\text{NH}_3$  and  $\text{H}_2\text{S}$  which immediately forms elementary sulfur by reaction with  $\text{SO}_2$ . The formation and decomposition of other intermediate compounds like  $(\text{NH}_4)_2\text{S}_n\text{O}_x$  ( $n = 2, x = 3$  and  $n = 3, x = 6$ ) results in the same decomposition products ( $\text{S}$ ,  $\text{SO}_2$  and  $\text{NH}_3$ ). Two basic iron sulfates, formed in different ratios during synthesizing experiments performed under  $\text{N}_2$  or in the presence of air, have been detected as solid intermediates which contain ammonium ions. The final decomposition product was proved to be  $\alpha\text{-Fe}_2\text{O}_3$  (mineral name hematite).

**Keywords** Ammonium hydroxydisulfiteferrate(III) · Thermal studies · Mössbauer spectroscopy · Decomposition · Redox reaction

## Introduction

In continuation of our efforts to synthesize and study compounds containing redox-active anionic and cationic components reacting with each other during heating in

quasi-intramolecular redox reactions [1–8], we have synthesized the diammonium *catena*-{bis( $\mu^2$ -sulfito- $\kappa\text{O},\kappa\text{O}$ )- $\mu^2$ -hydroxo- $\kappa^2\text{O}$ }ferrate(III) monohydrate (*i.e.*, ammonium disulfitehydroxoferrate, chemical formula  $(\text{NH}_4)_2[\text{Fe}(\text{OH})(\text{SO}_3)_2]\cdot\text{H}_2\text{O}$ ), abbreviated throughout the paper as compound **1**. Its thermal decomposition process and decomposition products were studied by TG-MS, XRD, IR, Raman and Mössbauer spectroscopy. Compound **1** was prepared by Erämetsä and Valkonen [9, 10] first; however,

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s10973-017-6901-4>) contains supplementary material, which is available to authorized users.

✉ László Kótai  
kotai.laszlo@ttk.mta.hu

<sup>1</sup> Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar Tudósok krt. 2, Budapest 1519, Hungary

<sup>2</sup> Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, Trg Dositaja Obradovića 3, Novi Sad 21000, Serbia

<sup>3</sup> János Szentágothai Research Centre, University of Pécs, Ifjúság útja 20, Pécs 7624, Hungary

<sup>4</sup> Institute of Chemistry, ELTE Eötvös Lorand University, Pázmány Péter sétány 1/A, Budapest 1117, Hungary

<sup>5</sup> Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Műegyetem rakpart 3, Budapest 1111, Hungary

<sup>6</sup> Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, Budafoki út 8, Budapest 1111, Hungary

<sup>7</sup> Institute of Mineralogy and Crystallography, Universität Wien, Althanstraße 14 (UZA 2), 1090 Vienna, Austria

<sup>8</sup> Faculty of Earth Science and Engineering, The University of Miskolc, Miskolc-Egyetemváros 3515, Hungary

<sup>9</sup> Department of Chemistry, Deogiri College, Station Road, Aurangabad, MS 431 005, India

the characterization of the reaction product was limited, and the thermal properties were not known at all. Therefore, compound **1** was synthesized; for pure material, the thermally initiated decomposition and the identity of decomposition intermediates were investigated.

## Experimental

As insert for the synthesis experiments served the chemical grade Sigma-Aldrich products iron(III) chloride hexahydrate and 25% aqueous ammonia solution. In addition, liquified SO<sub>2</sub> in 99.9% purity was supplied in a pressurized bottle by Unikén Ltd., Kecel, Hungary.

The synthesis of compound **1** was performed by the reaction of freshly prepared FeO(OH) with SO<sub>2</sub> in the presence of concentrated aqueous ammonia solution at 60 °C [9, 10]. The formed product, however, always contained impurities. The reason for the by-product formation is assigned to the local overheating of the reaction mixture (65–70 °C) due to the exothermic reaction of the excess of ammonia and sulfur dioxide gas; thus, the method was slightly modified. A long vertical tube equipped with gas inlet and outlet tubes was filled with 50 mL of a 4 M FeCl<sub>3</sub> solution, which was mixed with 100 mL of 25% aqueous NH<sub>3</sub> under vigorous stirring when a dark brown precipitate was formed. The mixture was warmed to 50 °C; SO<sub>2</sub> gas was simultaneously blown into the suspension. As soon as a white ammonium sulfite smoke leaked, the addition of the gas was interrupted. This procedure was repeated several times until any escape of smoke stopped. Then, the gas was blown in again, the temperature was not allowed to exceed 60 °C, and the mixture was shaken intensively. If the temperature started decreasing, it was adjusted to 60 °C by gentle heating. The SO<sub>2</sub> insufflation was continued until the whole mixture became egg-yellow in color and the dark brown iron-oxide hydroxide completely disappeared. The mixture was quickly filtered in air, and the reaction product was dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>. Due to the creamy character of the freshly prepared product, the drying process in the open air took a long time; after 15–20 min of drying, a brown layer of the decomposition product appeared on the surface. Elemental compositions of the starting material and decomposition intermediates (Fe and S content) were determined by ICP-AES with an Atomscan 25 instrument (Thermo Jarrel Ash, USA).

FT-IR spectra of solid samples were recorded in the attenuated total reflection (ATR) mode on a Bruker Alpha FT-IR spectrometer at 2-cm<sup>-1</sup> resolution.

X-ray powder diffraction measurements were taken using a Philips PW-1050 Bragg–Brentano parafocusing goniometer. It was equipped with a Cu tube operated at 40-kV and 35-mA tube power, a secondary beam graphite

monochromator and a proportional counter. Scans were recorded in step mode. Evaluation of the diffraction patterns had been obtained by full profile fitting techniques. Thermal data were collected using TA Instruments SDT Q600 thermal analyzer coupled to Hiden Analytical HPR-20/QIC mass spectrometer. The decomposition was followed from room temperature to 780 °C at 5 °C min<sup>-1</sup> heating rate in argon and air as carrier gas (flow rate = 50 cm<sup>3</sup> min<sup>-1</sup>). Sample holder/reference: alumina crucible/empty alumina crucible. Sample mass ~ 7 mg. Selected ions between *m/z* = 1–120 were monitored in multiple ion detection mode (MID).

The Raman measurements were taken using Horiba Jobin–Yvon LabRAM-type microspectrometer with external 532-nm Nd-YAG laser source (~ 40mW) and Olympus BX-40 optical microscope. The laser beam was focused by an objective of 10×. A D1 intensity filter decreased the laser power to 10% to avoid the thermal degradation. The confocal hole of 1000 μm and 1800 groove mm<sup>-1</sup> grating monochromator were used in a confocal system and for light dispersion. The spectral range of 100–4000 cm<sup>-1</sup> was detected as the relevant range with 3-cm<sup>-1</sup> resolution. Each spectrum was collected 240 s per point.

The Mössbauer spectra were measured at room temperature using a Mössbauer spectrometer (Ranger) in constant acceleration mode with a <sup>57</sup>Co(Rh) source of 0.2 GBq activity. Isomer shifts are given relative to an alpha iron at room temperature. The Mössbauer spectra were analyzed assuming Lorentzian line shapes with the help of the Mosswin 3.0i XP software.

## Results and discussion

### Synthesis and properties

Compound **1** was prepared by a slightly modified method as suggested by Erämetsä and Valkonen [9, 10] based on the reaction of 4 M FeCl<sub>3</sub>, 25% aq. NH<sub>3</sub> and SO<sub>2</sub> gas at 60 °C. The thus-obtained compound **1** was proved to be sufficiently pure, while compound **1a** obtained by the original method always contained further ammonium iron sulfite impurities. Avoidance of overheating due to the reaction heat was a key parameter in the preparation of the pure sample. There are good correlations between the powder XRD and IR data for the compound (NH<sub>4</sub>)<sub>2</sub>Fe(OH)(SO<sub>3</sub>)<sub>2</sub> given by Erämetsä and Valkonen [9, 10] and our results for compound **1**, but some further characteristics of the data of the impure sample differ. Most conspicuous is the incorporation of solvate water that was missing by the earlier authors. Consequently, the chemical formula has to be changed to (NH<sub>4</sub>)<sub>2</sub>Fe(OH)(SO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O.

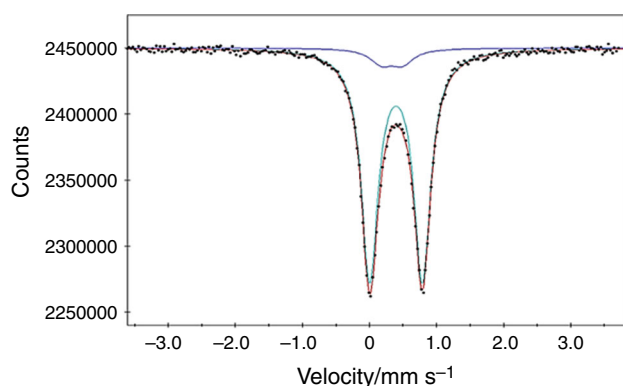
**Table 1** Cell parameters of compound **1**

|   | This work (powder XRD) | Erämetsä and Valkonen [9]           |
|---|------------------------|-------------------------------------|
| Crystal system                          | Orthorhombic           | Orthorhombic                        |
| $a$ (Å)                                 | 17.781                 | 8.912                               |
| $b$ (Å)                                 | 7.375                  | 10.677                              |
| $c$ (Å)                                 | 7.109                  | 11.821                              |
| $V$ (Å <sup>3</sup> )                   | 932.33                 | 1124.81                             |
| $Z$                                     | 4                      | 5                                   |
| Space group                             | Cmc <sub>21</sub>      | Not given                           |
| $d_{\text{calc}}$ (g cm <sup>-3</sup> ) | 2.034                  | 1.98 ( $d_{\text{exp}} = 1.91$ [9]) |

Erämetsä and Valkonen [9, 10] gave an orthorhombic unit cell that could be proved during the present work. However, the earlier given cell parameter resulted in a too large unit cell volume with a cell content  $Z = 5$  instead of  $Z = 4$  (Table 1). The XRD peak positions of compound **1** (Fig. S1) agreed well with the data of [9, 10]. The cell parameters are given in Table 1.

The Mössbauer spectrum of compound **1** with isomer shift,  $\delta = 0.392$  (1) mm s<sup>-1</sup>, and quadrupole splitting,  $\Delta = 0.784$  (1) mm s<sup>-1</sup> (Fig. 1), is consistent with an octahedral oxygen-coordinated high-spin iron(3+) species. A minor (8%) impurity component has not been identified. From these parameters, the polymeric nature of the compound with bridging sulfite or hydroxo groups has to be supposed instead of the S-bound monodentate coordination mode [9, 10].

The infrared bands of compound **1** (Fig. S2) agreed well with the data compiled by Erämetsä and Valkonen [9, 10] for (NH<sub>4</sub>)<sub>2</sub>Fe(OH)(SO<sub>3</sub>)<sub>2</sub>. All four normal modes of the trigonal pyramidal sulfite ion, i.e.,  $\nu_3(\text{E})$ ,  $\nu_1(\text{A}_1)$ ,  $\nu_2(\text{A}_1)$  and  $\nu_4(\text{E})$  [11, 12], are observable in the IR spectra of compound **1** (Fig. S2). They are tentatively assigned to absorption bands at 822 cm<sup>-1</sup> ( $\nu_1$ , S–O), 646 cm<sup>-1</sup> ( $\nu_2$ , S–O), 887 and 1017 cm<sup>-1</sup> ( $\nu_3$ , S–O, splitting is due to the bridging  $\kappa\text{O}$ ,  $\kappa\text{O}$  coordination and the low  $C_s$  symmetry of the sulfite ion) and at 505 cm<sup>-1</sup> ( $\nu_4$ , S–O).

**Fig. 1** Mössbauer spectrum of compound **1** at room temperature

The deformation bands of the bridged hydroxyl group were assigned at 1123 cm<sup>-1</sup>, while deformation bands of ammonium ion and solvate water appeared at 1443 and 1637 cm<sup>-1</sup>, respectively. The stretching band of OH occurs at 3506 cm<sup>-1</sup>, and the other (stretching and overtones) OH and NH bands appear around 2862, 2978, 3086 and 3165 cm<sup>-1</sup>, including shoulders. Further overtones/combination bands were observed between 1700 and 2500 cm<sup>-1</sup>.

## Thermal behavior

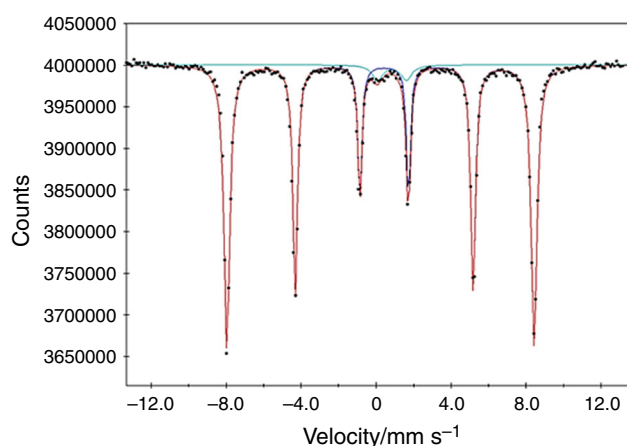
The dry compound **1** was proved to be stable in air in spite of well-known redox reaction between sulfites and iron(III) ions in aq. phases [13] because the bridging sulfite ions link the iron(III) centers into a polymeric chain giving an unusual stability for compound **1**. As it can be seen in Fig. S3a and in Table 2, the complete thermal decomposition process in inert atmosphere gave 73.00% mass loss, which is in good agreement with the formation of  $\alpha\text{-Fe}_2\text{O}_3$  as final decomposition product. (The theoretical value is 72.13%.) In air, this value was 70.46%. The presence of  $\alpha\text{-Fe}_2\text{O}_3$  (hematite) as decomposition product in N<sub>2</sub> atmosphere was unambiguously confirmed by Mössbauer spectroscopy ( $\delta = 0.334$  (2) mm s<sup>-1</sup>;  $\varepsilon = -0200$  (1) mm s<sup>-1</sup>,  $B = 51.01$  (2) T, Fig. 2) and XRD (Suppl. 4).

Despite the inert atmosphere and the presence of reducing sulfur(IV) species, the Mössbauer study showed only 3.5 and 4% of iron(II) in the decomposition intermediate (Suppl. 5a and 5b) and in the final decomposition product at 800 °C, respectively (for this latter:  $\delta = 0.85$  (2) mm s<sup>-1</sup>;  $\Delta = 1.55$  (3) mm s<sup>-1</sup>, Fig. 2). Thus, the expected redox reaction between the oxidizing central iron(III) and reducing ligand (sulfite) has no key role in the decomposition. For this minor iron(II) species, the low isomer shift may indicate lower coordination (e.g., four-coordinate iron) or coordinated sulfur instead of oxygen.

The thermal decomposition of compound **1** has two main stages. At least three decomposition processes are superposed by heating both under an inert atmosphere and

**Table 2** Thermal decomposition of compound **1** under Ar and air atmosphere (5 K min<sup>-1</sup> heating rate)

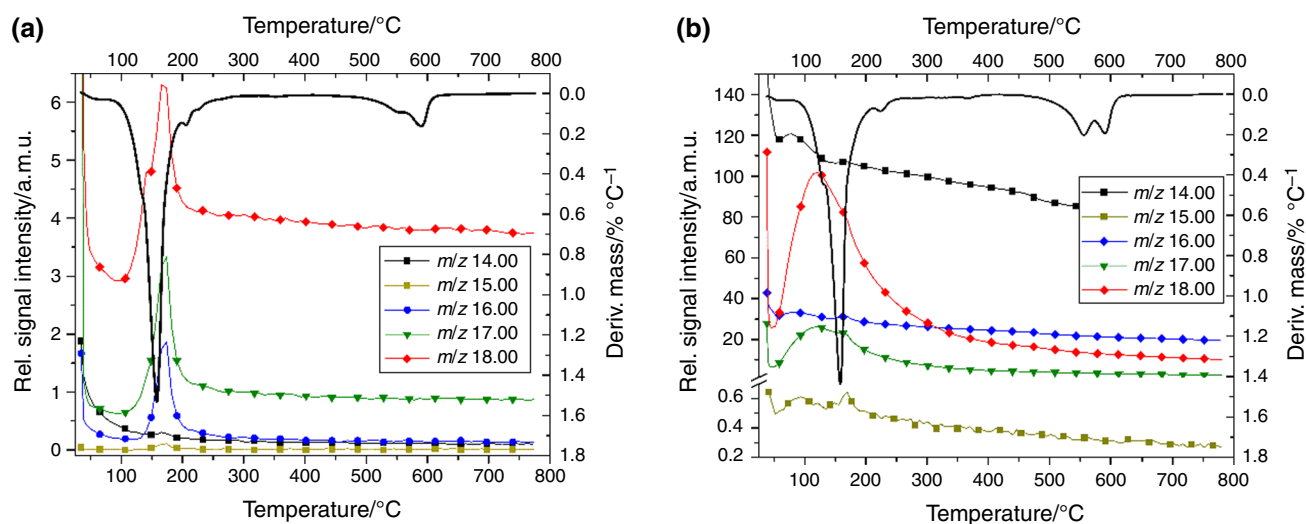
| Stage                   | Temp. range/°C | Peak temp./°C |                         | Mass loss/% | MS fragments  |
|-------------------------|----------------|---------------|-------------------------|-------------|---|
|                         |                | DTG           | DSC                     |             |   |
| <i>Inert atmosphere</i> |                |               |                         |             |   |
| 1                       | 99.5–222       | 157.7         | 162.8                   | 60.19       | SO <sub>2</sub> , S <sub>2</sub> , NH <sub>3</sub> , H <sub>2</sub> O, NO, S, N <sub>2</sub>                  |
| 2                       | 502–606        | 550.4         | Merged to the main peak | 12.81       |   |
|                         |                | 591.3         | 593.1                   |             |   |
| <i>Air</i>              |                |               |                         |             |   |
| 1                       | 104–241        | 158           | 161.6                   | 55.61       | SO <sub>2</sub> , S <sub>2</sub> , NH <sub>3</sub> , H <sub>2</sub> O, NO, N <sub>2</sub> O, H <sub>2</sub> S |
| 2                       | 522–607        | 556           | 558.3                   | 14.85       |   |
|                         |                | 593           | 594.5                   |             |   |

**Fig. 2** Mössbauer spectrum of the thermal decomposition product of compound **1** at 800 °C under N<sub>2</sub> stream

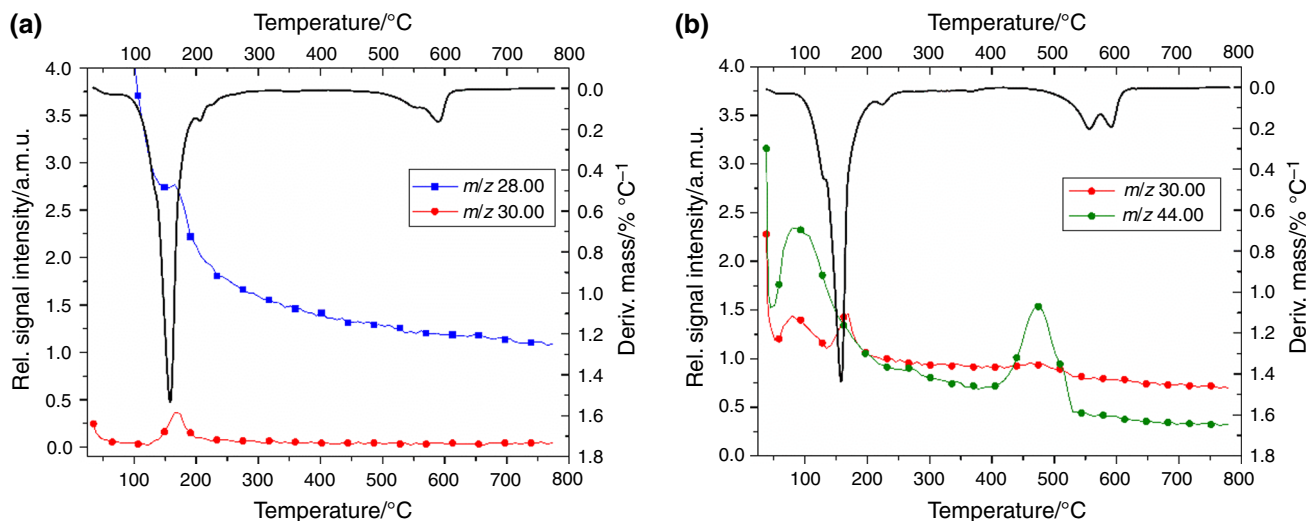
in air. Starting from about 100 °C crystalline water is lost. The DTG peak temperatures are centered around 130, 160 and 207/225 °C (under Ar/in air). These decomposition phases could not be separated. And the total mass loss of this stage is 60.19/55.91% in Ar and air, respectively. The mass loss in the second decomposition stage was found to be 12.81% in inert atmosphere and 14.85% in air. As the formula weight of (NH<sub>4</sub>)<sub>2</sub>Fe(OH)(SO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O is 287 g mol<sup>-1</sup>, it corresponded to only ~ 37/~ 42 g of lost gases from one mole of the title compound in Ar/air, respectively. This demonstrates the non-stoichiometric and/or multiphase composition of the intermediate reaction products formed in the first heating stage. The gas-phase composition monitoring by MS during the thermal decomposition of compound **1** showed almost the same main gaseous decomposition products (sulfur dioxide, water and ammonia) in both experiments (Figs. 3–5; Table 2).

Dehydration is performed in at least two consecutive steps; one results from the crystalline water (~ 130 °C), the other from the hydroxyl group (~ 170 °C). Some amount of water was formed during the oxidation reaction of ammonia in air ( $m/z = 30$  (NO) and  $m/z = 44$  (N<sub>2</sub>O)). A larger amount of N<sub>2</sub>O was formed from the ammonium ion containing basic iron sulfate intermediates around 480 °C: The oxidic iron compound probably catalyzed the aerial oxidation of the ammonia or the ammonium ion [14]. The mechanism of NH<sub>3</sub> oxidation differs in experiments performed under the inert atmosphere and in the presence of air. There is no N<sub>2</sub>O evolution under the inert atmosphere, but NO ( $m/z = 30$ ) and N<sub>2</sub> ( $m/z = 28$ ) formation could be detected. The oxidant in the inert atmosphere might be iron(III)-oxide compounds which could be responsible for the formation of the small amount of iron(II) that was present in the final decomposition product.

The solid decomposition intermediates and a white sublimate were studied by IR, XRD and Raman techniques. These intermediates and sublimate were obtained after isotherm heating of compound **1** in air or N<sub>2</sub> in a quartz tube at 300 °C. In the iron-containing intermediates, the presence of sulfates and elementary sulfur could be verified (Figs. S6 and S7). A ~ 6:1 mixture of ammonium sulfite and ammonium sulfate was found in the sublimate (Figs. S8 and S9). These reaction products are an unambiguous evidence for an auto-redox process with a partial oxidation and reduction of the sulfite ions. Since the iron(III) ion is not involved in this redox reaction, the appearance of redox products could only be attributed to the disproportionation of the ammonium sulfite. As a result, ammonium sulfate and at least one compound containing sulfur with less than four valence, probably an ammonium salt of H<sub>2</sub>S<sub>n</sub>O<sub>m</sub> ( $n = 2–6$ ,  $m = 3–6$ ) acids [15] (Fig. 6) are formed. However, the primarily formed sulfur-containing species could easily transform into other species, e.g., into elementary sulfur. The S-containing



**Fig. 3** DTG curves and TG-MS ion intensities for H<sub>2</sub>O- and NH<sub>3</sub>-containing products formed during thermal decomposition of compound **1**. **a** Under Ar, **b** under air



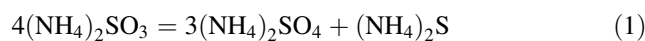
**Fig. 4** DTG curves and TG-MS ion intensities for NH<sub>3</sub>-oxidation products formed during thermal decomposition of compound **1**: **a** under Ar; **b** under air

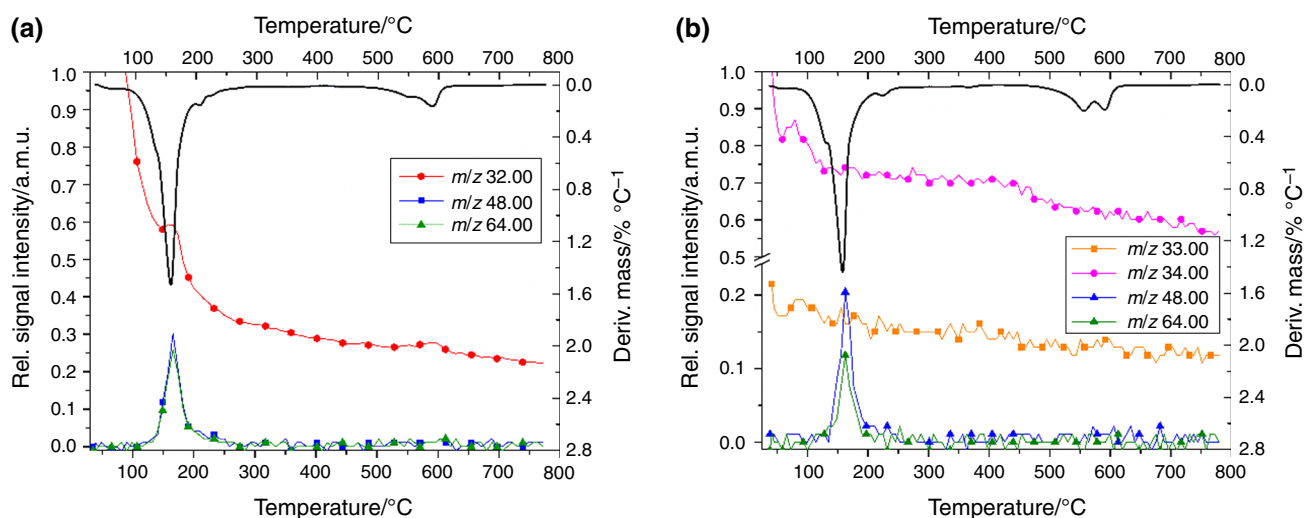
ions/molecules with intermediate oxidation states shown in Fig. S7 could disproportionate (reduce or oxidize) with the formation of a species with a higher (toward to the left) and another one with a lower (toward to the right) oxidation number. As it could be seen from Fig. 6, the primary disproportionation products of sulfites like thiosulfate or trithionate might also decompose further again into sulfur(IV) compounds (formation as SO<sub>2</sub>) and with the formation of even lower oxidation compounds (compound located at right).

It is well known that sulfites could disproportionate into sulfates and sulfides; for example, sodium sulfite and pyrosulfite decompose with disproportionation into sodium sulfate and sodium sulfide around 170 °C without mass

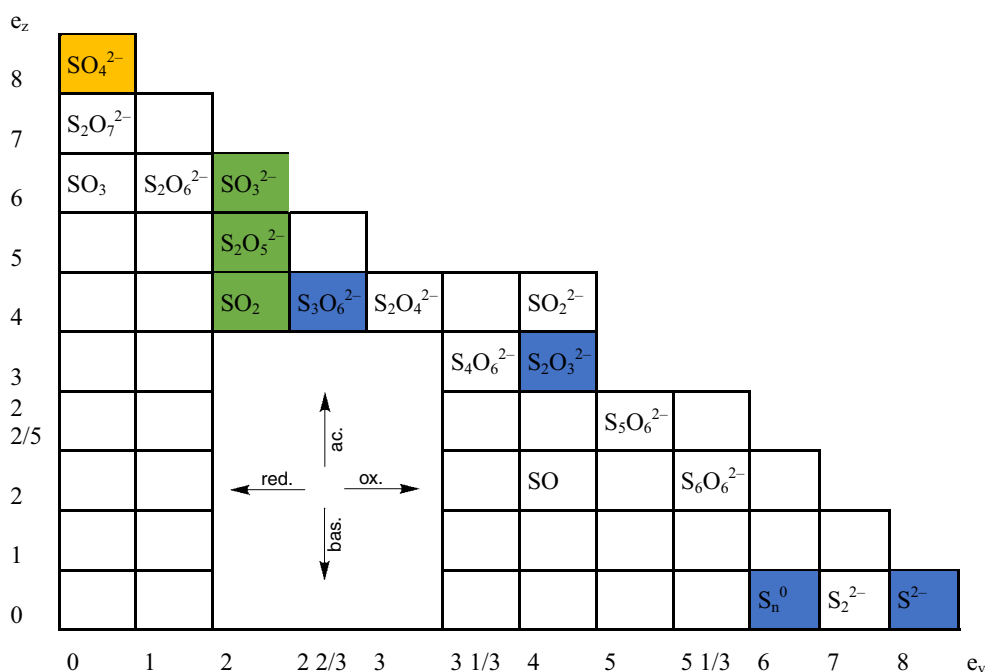
change [15, 16]. Transition metal sulfites also decomposed into the appropriate sulfide and sulfate mixture even in the presence of air [17], while under N<sub>2</sub> iron(II) sulfite gave iron(II) sulfate, magnetite and FeS<sub>2</sub> [18].

An analogous reaction of ammonium sulfite formed in the decomposition reaction of **1** could be expected to give ammonium sulfate and ammonium sulfide (Eq. 1). Ammonium sulfate was found in the white sublimate formed during heating. However, ammonium sulfide is not stable and decomposes above room temperature.





**Fig. 5** DTG curves and TG-MS ion intensities for S-containing products formed during thermal decomposition of compound **1**: under Ar **a**, under air **b**



**Fig. 6** Compilation of sulfur-containing molecules and anion groups that might be formed during the thermal decomposition of **1**.  $e_v$  (abscissa): formal number of free electrons normalized to one sulfur atom;  $e_z$  (ordinate): formal number of electric charges normalized to one sulfur atom. Color codes: green—redox-active disproportionating

species; yellow—isolable oxidation product; blue—reduced species; light blue—undetectable unstable intermediates; dark blue—neutral molecules or ammonium salts of sulfur-containing acids [15–22]. (Color figure online)

Therefore, only its decomposition products like  $\text{H}_2\text{S}$  and  $\text{NH}_3$  are detectable (Eq. 2). Accordingly, the evolution of  $\text{NH}_3$  ( $m/z = 17$  and fragments of it in decreasing intensity at  $m/z = 16, 15$  and  $14$ ) was observed on TG-MS both in the air and under the inert atmospheres. The regular decomposition reaction of compound **1**, however, also results in the formation of  $\text{NH}_3$ . Therefore, it was not

possible to distinguish between the ammonia formed from  $(\text{NH}_4)_2\text{S}$  or directly from compound **1**. It has to be mentioned that the peaks of  $m/z = 17$  and  $16$  contain the contributions of  $\text{NH}_3/\text{OH}$  and  $\text{NH}_2/\text{O}$  (and double-ionized S), while the  $m/z = 15$  exclusive fragments belong to  $\text{NH}_3$ . The peak at  $m/z = 14$  might belong to N atoms or result from  $\text{NH}_3$  or  $\text{NO}/\text{N}_2\text{O}$  fragmentations as well.  $\text{H}_2\text{S}$  ( $m/z = 34$ ) was expected as decomposition product. The MS

**Table 3** Distinctive relative intensities of  $m/z$  values of analyzed gases according to database available in the mass spectrometer Netzsch QMS 403C and <http://webbook.nist.gov/>

| $m/z$ | Ar/% | SO <sub>2</sub> /% | N <sub>2</sub> /% | NH <sub>3</sub> /% | H <sub>2</sub> O/% | N <sub>2</sub> O/% | NO/% | NO <sub>2</sub> /% | H <sub>2</sub> S/% |
|-------|------|--------------------|-------------------|--------------------|--------------------|--------------------|------|--------------------|--------------------|
| 14    | –    | –                  | 7.2               | 2.2                | –                  | 12.9               | 7.5  | 9.6                | –                  |
| 15    | –    | –                  | –                 | 7.5                | –                  | –                  | 2.4  | –                  | –                  |
| 16    | –    | 11.4               | –                 | 80.1               | 1.1                | 5.0                | 1.5  | 22.3               | –                  |
| 17    | –    | –                  | –                 | 100                | 23.0               | –                  | –    | –                  | –                  |
| 18    | –    | –                  | –                 | –                  | 100                | –                  | –    | –                  | –                  |
| 20    | 20   | –                  | –                 | –                  | –                  | –                  | –    | –                  | –                  |
| 28    | –    | –                  | 100               | –                  | –                  | 10.8               | –    | –                  | –                  |
| 30    | –    | –                  | –                 | –                  | –                  | 31.1               | 100  | 100                | –                  |
| 32    | –    | 10.4               | –                 | –                  | –                  | –                  | –    | –                  | 44.4               |
| 33    | –    | –                  | –                 | –                  | –                  | –                  | –    | –                  | 42.0               |
| 34    | –    | –                  | –                 | –                  | –                  | –                  | –    | –                  | 100                |
| 35    | –    | –                  | –                 | –                  | –                  | –                  | –    | –                  | 2.5                |
| 36    | –    | –                  | –                 | –                  | –                  | –                  | –    | –                  | 4.2                |
| 40    | 100  | –                  | –                 | –                  | –                  | –                  | –    | –                  | –                  |
| 44    | –    | –                  | –                 | –                  | –                  | 100                | –    | –                  | –                  |
| 46    | –    | –                  | –                 | –                  | –                  | –                  | –    | 37.0               | –                  |
| 48    | –    | 49.3               | –                 | –                  | –                  | –                  | –    | –                  | –                  |
| 64    | –    | 100                | –                 | –                  | –                  | –                  | –    | –                  | –                  |

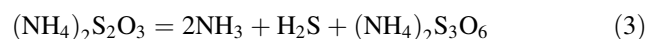
intensities of each fragment origin from different sources are summarized in Table 3.

However, it was not detected during heating experiments in inert atmosphere; in air traces of HS ( $m/z = 33$ ) and H<sub>2</sub>S ( $m/z = 34$ ) were detected. Since H<sub>2</sub>S immediately could react with the large amount of SO<sub>2</sub> resulting in the formation of elementary sulfur, the S<sub>*n*</sub> ( $n = 1–8$ ) species and other gaseous sulfur variants [19] should be monitored instead.

Accordingly, a signal at  $m/z = 64$  may belong to SO<sub>2</sub> and S<sub>2</sub> as parental species; also SO ( $m/z = 48$ ) and monoatomic S ( $m/z = 32$ ) as fragment ions of SO<sub>2</sub> and S<sub>2</sub>, respectively, could be detected. In air  $m/z = 32$  could not be allocated to any reaction product due to the complete overlap of aerial O<sub>2</sub>. The ratios of the signal intensities resulting from the components SO<sub>2</sub> + S<sub>2</sub> ( $m/z = 64$ ) and SO ( $m/z = 48$ ) in air and inert atmosphere, respectively, differ, i.e.,  $I_{64}/I_{48}$  was found to be  $\sim 1$  under argon, but it was  $\ll 1$  in air. It could be attributed to the distinct amount of SO<sub>2</sub> and S<sub>2</sub> formed in the air and under the inert atmosphere. SO was supposed to originate exclusively from the fragmentation of SO<sub>2</sub>. As the fragmentation obviously is independent on the distinct atmosphere, the SO<sub>2</sub>/SO ratio might be attributed to a decrease in S<sub>2</sub> accompanied by an increase in SO<sub>2</sub> contributing to the intensity of the  $m/z = 64$  peak. (Oxidation of S<sub>2</sub> in the air results into the formation of SO<sub>2</sub>.) Actually, S<sub>2</sub> was detected at the temperatures close to the decomposition temperature (170 °C) of compound **1** [19, 20].

The overall decomposition process is very complex due to the reaction of the intermediate products ammonia,

sulfur dioxide and water forming ammonium sulfite. In this reaction, the formation of ammonium sulfite was always accompanied by the formation of some amounts of ammonium thiosulfate and elementary sulfur [21]. Ammonium thiosulfate itself decomposes into NH<sub>3</sub>, SO<sub>2</sub>, hydrogen sulfide and ammonium trithionate at 150 °C at low heating rates (Eq. 3); during fast heating NH<sub>3</sub>, S and ammonium sulfate are formed [22]. The ammonium trithionate also decomposes at 160–170 °C forming analog reaction products [23].

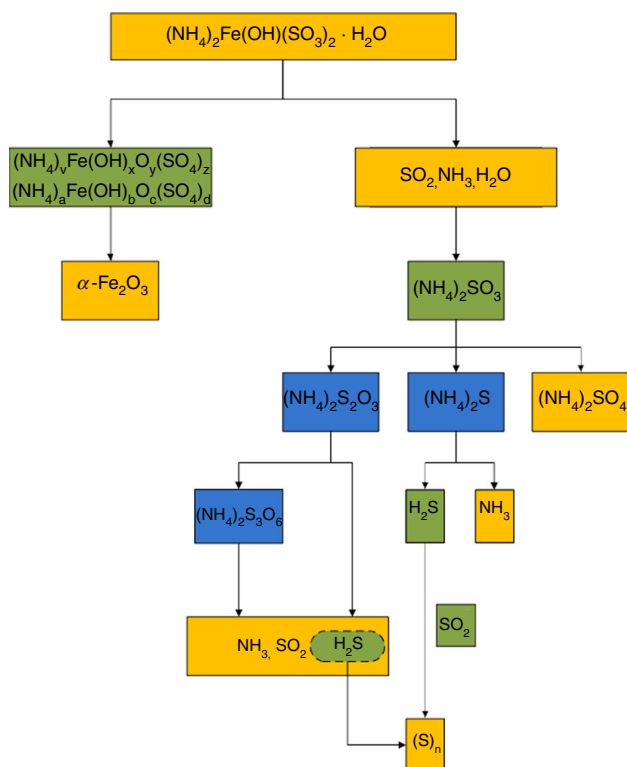


Since the decomposition temperatures of ammonium thiosulfate, trithionate and other polythionates are within the range of that of compound **1** ( $\sim 150$  to  $170$  °C), only the decomposition products (S, SO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>) of these possible intermediate compounds could be observed. Raman spectra of solid iron-containing intermediates confirm the presence of sulfur (Fig. S10). The three most intense absorption bands are allocated to S<sub>*n*</sub> species [24]; they occur at 143 ( $\nu_8$ , e, torsion), 218 ( $\nu_2$ , a<sub>1</sub>, bending) or 484 ( $\nu_1$ (a<sub>1</sub>) and  $\nu_7$ (e<sub>2</sub>), stretching) cm<sup>-1</sup> in both cases. The summarized possible reaction routes are presented in Fig. 7.

### The chemical nature of solid intermediates

Two types of intermediates were formed during the thermal decomposition of compound **1** both in air and in inert atmosphere; i.e., an iron-containing residue and a sublimate containing an ammonium sulfite and an ammonium sulfate.

The Mössbauer spectra of the former intermediate (Fig. S5) showed the presence of two iron(III) environments in a  $\sim 3:1$  and  $\sim 3:2$  ratio for the experiments under  $N_2$  and air; the iron to sulfur atomic ratio was 2.15:1 and 1.25:1, respectively, as detected by ICP measurements. These intermediates were supposed to be a two-component mixture of basic iron sulfate compounds; at least one of them



**Fig. 7** The supposed decomposition routes of compound **1**. Green: redox-active and disproportionating species; yellow: isolable products; blue: non-isolable reduced species. (Color figure online)

must contain ammonium ions as well. The different ratios reflect the distinct atmospheres. Since the presence of oxygen is proposed to oxidize  $SO_2$  formed during the first decomposition step in the presence of iron oxides [14], a larger amount of sulfur might be retained as sulfate in the sample investigated under air. Thus, the amount of the sulfur-rich iron sulfate phase must be higher as compared to the decomposition under the inert atmosphere. Therefore, the Mössbauer doublet with  $\delta = 0.34 \text{ mm s}^{-1}$  and  $\Delta = 1.34 \text{ mm s}^{-1}$  and the lower decomposition temperature on the DTG curve ( $\sim 550 \text{ }^\circ\text{C}$ ) might belong to the component richer in sulfur than the component decomposed at  $600 \text{ }^\circ\text{C}$  which gave Mössbauer parameters  $\delta = 0.36 \text{ mm s}^{-1}$  and  $\Delta = 0.81 \text{ mm s}^{-1}$ .

The intensity change of the DTG/DSC signal components at  $550/600 \text{ }^\circ\text{C}$  under Ar and air confirmed the different amounts of the two basic iron sulfates. (The Mössbauer and IR characteristics for the intermediates (Table 4) were proved to be almost the same for the two atmospheres.)

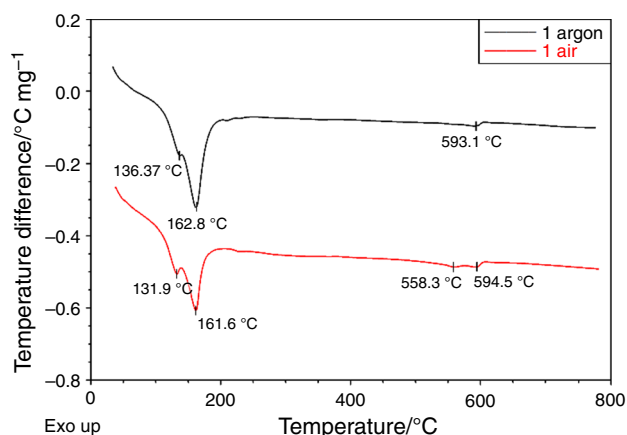
Numerous basic ammonium iron sulfate compounds like ammonium jarosites are known with similar IR, Mössbauer and thermal decomposition characteristics as we found in the case of the intermediates formed in our experiments [25–27].

The intermediates showed the presence of a bridged sulfate and a rotation-hindered ammonium ion. The appearance of the tentatively assigned  $\nu_1 + \nu_5$  combination band ( $\nu_5$  is a far-IR lattice band) is characteristic for a basic ammonium iron compound with polymerized sulfates and strong hydrogen bonds between the ammonium and oxide/sulfate ions. The absorption bands resulting from a bridging/complexed hydroxy group might be located at  $970$  to  $1000$  and  $1100 \text{ cm}^{-1}$  overlapping with the absorption bands of the sulfate ions. The absorption band around the

**Table 4** Wave numbers of the IR bands of decomposition intermediates of compound **1**

| Assignment  | Reaction under air   |                    | Reaction under $N_2$ |                    |
|---|----------------------|--------------------|----------------------|--------------------|
|   | IR/ $\text{cm}^{-1}$ | Relative intensity | IR/ $\text{cm}^{-1}$ | Relative intensity |
| $\nu_1$ and $\nu_3$ (NH) + $\nu$ (OH)                 | 3380                 | 0.44               | 3380                 | 0.26               |
| $\nu_3$ (NH)  | 3228                 | 0.43               | 3228                 | 0.29               |
| $\nu_1(A_1)$ (NH)                                     | 3072                 | 0.43               | 3075                 | 0.28               |
| $2\nu_4$ (NH)   | 2860                 | 0.41               | 2859                 | 0.25               |
| $\nu_2(E)$ (NH) or $\delta$ (OH)                      | 1633                 | 0.40               | 1632                 | 0.25               |
| $\nu_4(F_2)$ (NH)                                     | 1431                 | 0.43               | 1427                 | 0.30               |
| $\nu_3(F_2)$ (SO)                                     | 1183                 | 0.50               | 1196                 | 0.36               |
| $\nu_3(F_2)$ (SO)                                     | 1045                 | 0.611              | 1034                 | 0.53               |
| $\nu_1(A_1)$ (SO) or $\delta$ (OH <sub>bridge</sub> ) | 991                  | 0.57               | 998                  | 0.50               |
| $\nu_4(F_2)$ (SO)                                     | $\sim 650$           | Shoulder           | $\sim 650$           | Shoulder           |
| $\nu_4(F_2)$ (SO)                                     | 595                  | 0.64               | 587                  | 0.49               |
| $\nu_2(E)$ (SO)                                       | $\sim 450$           | 0.73               | $\sim 450$           | 0.53               |





**Fig. 8** DSC curves (simultaneous measurement with TG) of compound **1** in air and under Ar

$\delta(\text{OH})$  deformation band ( $1650\text{ cm}^{-1}$ ) is close to the  $\nu_2(\text{NH})$  absorption band; the upper combination bands might overlap with  $\nu(\text{OH})$  as well.

There was an important difference between the decomposition intermediate of pure **1** (synthesized during the present work) and contaminated sample (**1a**) prepared according to Erämettä and Valkonen [9, 10]. The decomposition of compound **1a** at  $300\text{ °C}$  (2 h,  $\text{N}_2$  atmosphere) resulted in two crystalline phases which could be identified as  $\text{NH}_4\text{Fe}(\text{SO}_4)_2$  (**2**) and  $(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$  (**3**) by XRD (Fig. S4). The IR spectra of the intermediates from compound **1** taken under analogous conditions were very similar, indicating that both materials contain ammonium and sulfate ions in similar chemical environments as in compounds **2** and **3**. However, the Mössbauer spectra (taken under air or  $\text{N}_2$ ) obtained from the decomposition intermediates from compound **1** and those from compounds **2** and **3** (synthesized according to [28, 29]) are quite different. Neither compound **2** nor compound **3** is formed during decomposition of compound **1**. The decomposition temperatures of compounds **2** and **3** are roughly around  $400$  and  $500\text{ °C}$ , respectively [14]. There was no decomposition step of the pure compound **1** at these temperatures. Thus, compounds **2** and **3** formed probably by a decomposition reaction of an unknown contaminant present in impure sample (**1a**) prepared by the original method given by [9, 10] (Fig. 8).

## Conclusions

1. The thermal decomposition of ammonium hydroxodisulfiteferrate(III), (diammonium *catena*-{bis( $\mu^2$ -sulfite-O,O)- $\mu^2$ -hydroxo}ferrate(III) monohydrate),  $(\text{NH}_4)_2[\text{Fe}(\text{SO}_3)_2\text{OH}]\cdot\text{H}_2\text{O}$ , is a two-stage (chemically multistep within each thermal decomposition stages)

process with the formation of two basic ammonium iron sulfate intermediates, whose relative amount differs for the samples prepared in an oxidizing or inert atmosphere.

2. The first decomposition stage is located between  $100$  and  $240\text{ °C}$ , the primary decomposition release  $\text{SO}_2$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , which form isolable ammonium sulfite intermediates in spite of the expected redox reaction between the iron(III) and sulfite ions. Only a marginal amount of iron(II) ions is formed (ca. 3.5–4 mol %). During the decomposition in an inert atmosphere, the final decomposition product is  $\alpha\text{-Fe}_2\text{O}_3$  (mineral name hematite).
3. The ammonium sulfite formed from  $\text{SO}_2$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  at the first decomposition step of **1** disproportionates, leading to the formation of ammonium sulfate and an unstable ammonium sulfide. The latter releases upon decomposition and reaction with  $\text{SO}_2$  elementary sulfur. The sulfur formation may take place in parallel with the decomposition of further by-products/intermediates such as ammonium thiosulfate or trithionate. These processes are superposed into one decomposition stage. The mass loss in the second decomposition stage is 12.81% in the inert atmosphere and 14.85% in air.

**Acknowledgements** J. Magyari thanks for supporting the research by Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 172014). I. M. Szilágyi thanks for a János Bolyai Research Fellowship of the Hungarian Academy of Sciences and an ÚNKP-17-4-IV-BME-188 Grant. An OTKA PD-109129 Grant, a VEKOP-2.3.2.-16-2017-00013 and a K 124212 Grant are acknowledged.

## References

1. Kótai L, Gács I, Sajó IE, Sharma PK, Banerji KK. Beliefs and facts in permanganate chemistry—an overview of the synthesis and the reactivity of simple and complex permanganates. *Trends Inorg Chem.* 2009;11:25–104.
2. Kotai L, Banerji KK, Sajó I, Kristof J, Sreedhar B, Holly S, Keresztury G, Rockenbauer A. An unprecedented-type intramolecular redox reaction of solid tetraamminecopper(2+) bis(permanganate) ( $[\text{Cu}(\text{NH}_3)_4](\text{MnO}_4)_2$ )—a low-temperature synthesis of copper dimanganese tetraoxide-type ( $\text{CuMn}_2\text{O}_4$ ) nanocrystalline catalyst precursors. *Helv Chim Acta.* 2002;85(8):2316–27. [https://doi.org/10.1002/1522-2675\(200208\)85:8<2316:AID-HLCA2316>3.0.CO;2-A](https://doi.org/10.1002/1522-2675(200208)85:8<2316:AID-HLCA2316>3.0.CO;2-A).
3. Kotai L, Fodor J, Jakab E, Sajó I, Szabo P, Lonyi F, Valyon J, Gacs I, Argay G, Banerji KK. A thermally induced low-temperature intramolecular redox reaction of bis(pyridine)silver(I) permanganate and its hemipyridine solvate. *Trans Metal Chem.* 2006;31(1):30–4. <https://doi.org/10.1007/s11243-005-6322-2>.
4. Sajó IE, Kotai L, Keresztury G, Gacs I, Pokol Gy, Kristof J, Soptrayanov B, Petrusovski VM, Timpu D, Sharma PK. Studies on the chemistry of tetraamminezinc(II) dipermanganate ( $[\text{Zn}(\text{NH}_3)_4](\text{MnO}_4)_2$ ): low-temperature synthesis of the

- manganese zinc oxide ( $ZnMn_2O_4$ ) catalyst precursor. *Helv Chim Acta*. 2008;91(9):1646–58. <https://doi.org/10.1002/hlca.200890180>.
- Kótai L, Sajó IE, Keresztury G, Németh CS, Gács I, Menyhár A, Kristóf J, Hajba L, Petrusevski VM, Ivanovski V, Timpu D, Sharma PK. Studies on the chemistry of  $[Cd(NH_3)_4](MnO_4)_2$ . A low-temperature synthesis route of the  $CdMn_2O_{4+x}$  Type  $NO_x$  and  $CH_3SH$  sensor precursors. *Z Anorg Allgem Chem*. 2012;638(1):177–86. <https://doi.org/10.1002/zaac.201100467>.
  - Hunyadi D, Sajó IE, Szilágyi IM. Structure and thermal decomposition of ammonium metatungstate. *J Therm Anal Calorim*. 2014;116:329–37.
  - Hunyadi D, Ramos ALVM, Szilágyi IM. Thermal decomposition of ammonium tetrathiotungstate. *J Therm Anal Calorim*. 2015;120:209–15. <https://doi.org/10.1007/s10973-015-4513-4>.
  - Nagy-Kovács T, Hunyadi D, de Lucena ALA, Szilágyi IM. Thermal decomposition of ammonium molybdates. *J Therm Anal Calorim*. 2016;124:1013–21. <https://doi.org/10.1007/s10973-015-5201-0>.
  - Erämetsä O, Valkonen J. Ammonium ferric sulfites. *Suomen Kemistilehti*. 1972;45(3):91–4.
  - Erämetsä O. Über Ammonisulfiterferriate. *Ann Acad Sci Fenn Ser A*. 1943;59:5–30.
  - Nakamoto K. Infrared and raman spectra of inorganic and coordination compounds, Part A and B. 5th ed. New York: Wiley Intersci Publications; 1997.
  - Newman G, Powell DB. The infra-red spectra and structures of metal sulfite compounds. *Spectrochim Acta*. 1963;19:213–24. [https://doi.org/10.1016/0371-1951\(63\)80100-9](https://doi.org/10.1016/0371-1951(63)80100-9).
  - Skorik NA, Zatulokina NA. Reaction of iron(III) with sulfite in various media. *Zh Neorg Khim*. 1986;31(9):2287–91.
  - Maxteed EB. The synthesis of ammonia and the oxidation of ammonia to nitric acid. *J Soc Chem Ind*. 1907;36:777–82. <https://doi.org/10.1002/jctb.5000361401>.
  - Jaszczak-Figiel B, Gontarz Z. Stages of thermal decomposition of sodium oxosalts of sulphur. *J Therm Anal Calorim*. 2009;96:147–54. <https://doi.org/10.1007/s10973-008-9195-8>.
  - Erdey L, Simon J, Gál S, Liptay G. Thermoanalytical properties of analytical-grade reagents—IVA: sodium salts. *Talanta*. 1966;13(1):67–80. [https://doi.org/10.1016/0039-9140\(66\)80127-3](https://doi.org/10.1016/0039-9140(66)80127-3).
  - Budkuley JS, Patil KC. Synthesis, infrared spectra and thermo-analytical properties of transition metal sulfite hydrazine hydrates. *J Therm Anal Calorim*. 1990;36:2583–92. <https://doi.org/10.1007/BF01913655>.
  - Bugli G, Pannettier G. Décomposition thermique du sulfite de fer(II) anhydre. *J Therm Anal Calorim*. 1979;16(2):355–63. <https://doi.org/10.1007/BF01910697>.
  - Meyer B. Elemental sulfur. *Chem Rev*. 1976;76(3):367–88. <https://doi.org/10.1021/cr60301a003>.
  - Startsev AN, Kruglyakova OV. Diatomic gaseous sulfur obtained at low temperature catalytic decomposition of hydrogen sulfide. *J Chem Chem Eng*. 2013;7:1007–13.
  - Applebey MP, Lanyon JA. The oxidation of ammonium sulphide. *J Chem Soc*. 1926. <https://doi.org/10.1039/JR9262902983>.
  - Rammelsberg C. Beiträge zur Kenntniss der unterschweflig-sauren Salze. *Pogg Ann*. 1842;132(6):295–323. <https://doi.org/10.1002/andp.18421320609>.
  - Divers E, Ogawa M. Products of heating of ammonium sulphites, thiosulphate and trithionate. *J Chem Soc Trans*. 1900;77:335–40. <https://doi.org/10.1039/CT9007700335>.
  - Trofimov BA, Sinogovskaya LM, Gusarova NK. Vibrations of the S–S bond in elemental sulfur and organic polysulfides: a structural guide. *J Sulfur Chem*. 2009;30(5):518–54. <https://doi.org/10.1080/17415990902998579>.
  - Frost RL, Wills R-A, Klopogge T, Martens W. Thermal decomposition of ammonium jarosite  $(NH_4)Fe_3(SO_4)_2(OH)_6$ . *J Therm Anal Calorim*. 2006;84(2):489–96. <https://doi.org/10.1007/s10973-005-6953-8>.
  - Lopez-Delgado A, Lopez FA. Thermal decomposition of ferric and ammonium sulfates obtained by bio-oxidation of water pickling liquors with *Thiobacillus ferrooxidans*. *J Mater Sci*. 1995;30:5130–8.
  - Majzlan J, Alpers CN, Bender Koch C, McCleskey RB, Myneni SCB, Neil JM. Vibrational, X-ray absorption, and Mössbauer spectra of sulfate minerals from the weathered massive sulfide deposit at Iron Mountain, California. *Chem Geol*. 2011;284:296–305. <https://doi.org/10.1016/j.chemgeo.2011.03.008>.
  - Garcia FJ, Rubio A, Sainz E, Gonzalez P, Lopez FA. Preliminary study of treatment of sulphuric pickling water waste from steel-making by bio-oxidation with *thiobacillus ferrooxidans*. *FEMS Microbiol Rev*. 1994;14:397–404. <https://doi.org/10.1111/j.1574-6976.1994.tb00114.x>.
  - Demartin F, Grammacioli CM, Campostrini I. Pyracmonite,  $(NH_4)_3Fe(SO_4)_3$ , a new ammonium iron sulfate from La Fossa, Crater, Vulcano, Aeolian Islands, Italy. *Can Mineralog*. 2010;48:307–13. <https://doi.org/10.3749/canmin.48.2.307>.