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Berg, Rolf W.; Ferré, Irene Maijó; Schäffer, Susan Jeanne Cline

Published in:
Vibrational Spectroscopy

Link to article, DOI:
10.1016/j.vibspec.2006.05.021

Publication date:
2006

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Raman spectroscopy evidence of 1:1:1 complex formation during dissolution of WO$_3$ in a melt of K$_2$S$_2$O$_7$\(\cdot\)K$_2$SO$_4$

Rolf W. Berg a,*, Irene Maijó Ferre a,b, Susan J. Cline Schäffer a

a Department of Chemistry, The Technical University of Denmark, Kemitorvet, Building 207, DK-2800 Lyngby, Denmark
b Facultat de Química, University of Rovira i Virgili, Tarragona 43007, Spain

Available online 21 June 2006

Abstract

Highly inert yellow solid WO$_3$ was found to be soluble in considerable amounts in molten K$_2$S$_2$O$_7$ at elevated temperatures (\(\sim 650 \, ^\circ\text{C}\)), if only similar molar amounts of sulfates were also present. The dissolution reaction of WO$_3$ into a melt consisting of a 1:1 molar mixture of K$_2$S$_2$O$_7$ and K$_2$SO$_4$ was studied in detail, and Raman spectroscopy was used to characterize the products. In combination with single crystal X-ray crystal structure determination, it was shown that a new dimeric compound, K$_8$\([\{\text{WO}_2\text{SO}_4\}_2\}\text{\{-SO}_4\}_2\], was formed and its assigned Raman spectrum at room temperature is given. The WO$_2^{2+}$ cores of the dimeric complex have their symmetrical and antisymmetrical stretching modes $\nu_1$\text{(WO}_2^{2+})$ at around 1054 (strong) and 1042 (weak), and the bending mode $\nu_2$\text{(WO}_2^{2+})$ at around 292 (medium intensity), respectively (positions given in cm$^{-1}$).

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Keywords: Assignment; Dissolution; K$_2$SO$_4$; K$_2$S$_2$O$_7$; K$_8$\([\{\text{WO}_2\text{SO}_4\}_2\}\text{\{-SO}_4\}_2\]; Melt; Raman; Solid; Spectroscopy; Tungsten oxide; WO$_3$

1. Introduction

Previously we have studied the dissolution properties of a number of oxide salts in disulfate (pyrosulfate) salt melts. In one case, Nb$_2$O$_5$ was found to dissolve in considerable amounts into molten K$_2$S$_2$O$_7$ at about 450 $^\circ\text{C}$ [1,2]. The stoichiometric properties of this and similar reactions were studied by Raman spectroscopy [3] and X-ray single crystal diffraction [4]. Other oxide salts, e.g. ZnO [5] and MoO$_3$ [6], were recently found to dissolve into Na$_2$S$_2$O$_7$ and K$_2$S$_2$O$_7$, and references to more systems are described there.

In this communication, we report results on tungsten oxide, WO$_3$. This oxide is known as a highly inert yellow solid compound that is practically insoluble in acids. This insolubility, combined with other properties, makes tungsten oxide itself and mixtures with other metal oxides commonly used catalysts or supported catalyst surfaces, see e.g. [7].

Recently we confirmed that WO$_3$ is sparingly soluble in acidic melts of K$_2$S$_2$O$_7$, but, surprisingly, we also discovered [8] that considerable amounts of WO$_3$ did dissolve in into melts of K$_2$S$_2$O$_7$ at elevated temperatures (~650 $^\circ\text{C}$) if similar amounts of sulfates (or possibly potassium oxide and SO$_3$) were also present. The purpose of the present project, therefore, was to use Raman spectroscopy to characterize the products formed by mixing WO$_3$, K$_2$SO$_4$ and K$_2$S$_2$O$_7$ in varying molar amounts in sealed ampoules, and then to study the range of stability of the products.

In the following, we will interpret the Raman spectra of the molten solutions to show that a 1:1:1 reaction:

$$\text{WO}_3 + \text{K}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_7 \rightarrow \text{products}$$

took place, and that [WO$_2$]$^{2+}$ ions solvated by SO$_4^{2-}$ ions are formed. The stoichiometry of the reaction was determined by isolating crystals and examining them by single crystal X-ray diffraction; the results were confirmed by Raman spectroscopy.

2. Experimental

2.1. Samples

The hygroscopic K$_2$S$_2$O$_7$ [7790-62-7] was synthesized from dried K$_2$S$_2$O$_3$ salt [7727-21-1] (Merck, pro analysi > 99%) by thermal decomposition at 250 $^\circ\text{C}$ for 1 h under a dry nitrogen atmosphere.
atmosphere [9]. The anhydrous product was immediately transferred to an air-filled dry box (the hygroscopic K2S2O7 requires handling in a dry box to avoid that it picks up water) [9]. In the box weighed amounts of WO3 (tungsten (VI) oxide [1314-35-8], Merck, reinst > 99%) and K2SO4 ([7778-80-5], Merck, suprapur > 99.999%), were mixed with K2S2O7 in varying molar amounts. The mixtures were introduced into cylindrical quartz ampoules that were subsequently removed from the dry box and immediately sealed under vacuum. The relative molar compositions are given in Table 1. A composition triangle diagram is shown in Fig. 1. The ampoules were heated for a few hours in a rocking furnace at ~650 °C, a temperature high enough for liquids to form (the m.p. of K2S2O7 is 419 °C [10]). The appearance of three samples after reaction is shown in Fig. 2.

2.2. Raman equipment

Raman spectra were obtained by use of a DILOR-XY 800 mm focal-length multi-channel spectrometer with macro- and micro-entrances (see Fig. 3). Excitation was done with filtered Ar+ ion laser light (wavelength 514.5 nm, power ~400 mW continuously, vertical polarization obtained by suitable rotation of the half-wave plate). The horizontal macro-entrance was used for the melts, and crystals were measured under the microscope. Filtration of Rayleigh scattering was done with a Kaiser holographic SuperNotch-Plus® filter or near the laser line with the double pre-monochromator. Depending on the selected grating, the Raman spectral resolution was within 2–8 cm⁻¹. The light was detected with a liquid N2-cooled CCD detector (140 K) connected to a MS Windows-98 computer with the Horiba-JobinYvon LABSPEC® software. A sheet polarization analyzer, permitting vertically (V) or horizontally (H) polarized light to pass, was used to obtain VV- and VH-polarized spectra of liquids. Calibration was done with cyclohexane and sulfur lines to a precision of 1 cm⁻¹ [11].

3. Results and discussion

By inspection through the furnace windows, it was found that WO3 dissolved (reacted) in considerable amounts in molten K2S2O7 + K2SO4 mixtures to form viscous yellowish melts, especially at high temperatures. When samples were cooled slowly, the melts froze to microcrystalline lumps (for low WO3 contents) and clear glasses (for higher WO3 contents) (see Fig. 2, bottom).

Equimolar amounts of K2S2O7, K2SO4 and WO3 gave clear homogeneous glass masses of gross formulae K4(WO2)(SO4)3. No chemical analysis was made, since the compositions were already known and the melts were homogeneous. No attack on the quartz wall was seen even after prolonged heating.

Crystals were grown by quenching the melts, partly remelting them and then cooling at a rate of 6 °C per hour, allowing for better crystallization. The ampoules were studied directly or, for crystallographic examination, broken and the
Fig. 3. Schematics of the Raman DILOR-XY spectrometer. M, mirror; λ/2, half-wave plate; IF, interference filter; L, lens; NF, notch filter; P, polarizer; G, grating. The furnace was mounted on a XYZ-table (not shown), allowing the melts to be placed at the sample position to the right.
colorless crystals taken out at ambient temperature. They proved to be quite stable in ordinary air. Single crystals of a compound, made from $1\text{WO}_3:1\text{K}_2\text{S}_2\text{O}_7:1\text{K}_2\text{SO}_4$, have recently been obtained, and the X-ray structures of a couple of crystals solved [8] to show that the dimeric compound, $\text{K}_8[\text{W}^{\text{VI}}\text{O}_2(\text{SO}_4)_2]_2(\mu-\text{SO}_4)_2$, is formed. The structure is shown in Fig. 4. The compound crystallizes in the monoclinic space group $P2_1/n$ with two dimeric units in the unit cell of dimensions $a = 9.4362 \text{ Å}, b = 13.9625 \text{ Å}, c = 10.1948 \text{ Å},$ and $\beta = 90.780^\circ$ [8].

The $(\mu-\text{SO}_4)_2$ way of linking of two $\text{MO}_2^{2+}$ centers (see Fig. 4, $\text{M} = \text{metal}$) has previously been found for molybdenum, where polymeric strands occurred by repetition of the linking in the $\text{K}_2\text{MoO}_2(\text{SO}_4)_2$ structure [6]. Here in the Mo-containing melts, bands assignable to $\nu_1(\text{C}_2n)$ in bridging sulfato groups were seen at 958 cm$^{-1}$ [6]. The W(VI) coordination sphere [8] shown in Fig. 4 is generated by inversion symmetry from the independent $[\text{W}^{\text{VI}}\text{O}_2(\text{SO}_4)_3]^{4+}$ moiety, resulting in two bridging sulfato ligands.

During this work, by varying the composition of the melt (Table 1) and isolating crystals, it was shown that the dimeric compound $\text{K}_8[\text{W}^{\text{VI}}\text{O}_2(\text{SO}_4)_2]_2(\mu-\text{SO}_4)_2$ exists from at least 5 to 29 mol% (see Fig. 1). Melting of the $\text{K}_8[\text{W}^{\text{VI}}\text{O}_2(\text{SO}_4)_2]_2(\mu-\text{SO}_4)_2$ crystals started at about 600 °C (visual observation).

### 3.1. Vibrational spectra

Raman spectra of melts at $\sim 650 \degree C$ and frozen solutions at $\sim 25 \degree C$ are shown in Figs. 5–8 ($X =$ formal mole fraction of $\text{WO}_3$ and $\text{K}_2\text{SO}_4$ in the $\text{WO}_3-\text{K}_2\text{SO}_4-\text{K}_2\text{S}_2\text{O}_7$ system, see Table 1).

The spectra of melts of different compositions (see Fig. 5) showed that the characteristic bands of $\text{K}_2\text{S}_2\text{O}_7$ gradually disappeared when the tungsten oxide content was increased. At the same time, new bands appeared monotonically, indicating that a reaction has occurred. More precisely, it was seen that the most characteristic 1086 cm$^{-1}$ band of $\text{K}_2\text{S}_2\text{O}_7$ disappeared and the new 1045 cm$^{-1}$ band of the mixture (the new compound)

![Fig. 5. Raman spectra of melts of different compositions ($X =$ formal mole fraction of $\text{WO}_3$ and $\text{K}_2\text{SO}_4$ in the $\text{WO}_3-\text{K}_2\text{SO}_4-\text{K}_2\text{S}_2\text{O}_7$ system) at $\sim 650 \degree C$ (spectra shifted in $y$-axis for clarity).](image)

![Fig. 6. Polarized Raman spectra of the melt of composition $X = 0.27$ ($X =$ formal mole fraction of $\text{WO}_3$ and $\text{K}_2\text{SO}_4$ in the $\text{WO}_3-\text{K}_2\text{SO}_4-\text{K}_2\text{S}_2\text{O}_7$ system) at $\sim 650 \degree C$. $\text{WO}_2^{2+}$ and $\text{SO}_4^{2-}$ stretches and $\text{WO}_2^{2+}$ bending can be assigned to bands at $\sim 1100$, $\sim 900$ and $\sim 390$ cm$^{-1}$. Other assignments are presented in Table 2. Spectra have been shifted in $y$-axis for clarity.](image)
increased with the WO₃ percentage. Even at the highest contents of tungsten oxide and sulfate (Fig. 6), we only saw indication of one kind of complex. In Fig. 6 the polarized Raman spectra of the melt of composition X = 0.27 is shown as an example. In Fig. 7, Raman spectra are presented of a K₂S₂O₇ melt, saturated with K₂SO₄, of the complex in the hot melt, of the complex in a frozen glassy K₂S₂O₇ "solvent", and of the microcrystalline frozen K₂S₂O₇ "solvent".

The reaction is accordingly interpreted as a formation of [WO₂]²⁺ ions solvated by bridging SO₄²⁻/C₀²⁻ ions. In the light of the X-ray results and the similarity of the spectra in the solid and dissolved state, the stoichiometry of the reaction is represented as 1:1:1, i.e. the reaction:

\[
2\text{WO}_3 + 2\text{K}_2\text{SO}_4 + 2\text{K}_2\text{S}_2\text{O}_7 \rightarrow 8\text{K}^+ + \left\{\text{W}^{\text{VI}}\text{O}_2\left(\text{SO}_4\right)\right\}_2\left(\mu\text{-SO}_4\right)_{28}^{-}
\]

Previously we have described [1,3] a method to determine the stoichiometry of such reactions. When trying to use the method here, by plotting the area ratios between these two bands (ν_{\text{disulfate}} = 1086 cm⁻¹, ν_{\text{compound}} = ~1045 cm⁻¹) versus composition (in Fig. 9) we see a decrease of the area ratio with the increase of the WO₃ concentration. The curve obtained is not straight; however, it extrapolates smoothly towards the 1:1:1 reaction product, as expected from the X-ray results.

3.2. Assignments

The positions of the fundamental bands of a regular free SO₄²⁻ ion of T₄₅ symmetry are well known: \(v_1 = 983, v_2 = 450, v_3 = 1105\) and \(v_4 = 611\) cm⁻¹ [12]. When the symmetry of the SO₄²⁻ ion is lowered by complex formation (Fig. 4), two different approximate symmetries for the sulfate ion have been found previously; \(C_{3v}\) (bound unidentately) and \(C_{2v}\) (bound bridged bidentately) with shifted vibrational frequencies [12]. The vibrational spectrum for the disulfate (pyrosulfate) ion is well known and well understood, based on recent ab initio calculations [13]. Therefore, the bands due to the SO₄²⁻ and S₂O₇²⁻ ions can be quite definitely identified.

The free bent [WO₂]²⁺ ion has three vibrational degrees of freedom. Under the C₂₅ point group symmetry, the fundamentals are expected at around: \(v_1 = 972, v_2 = 300\) and \(v_3 = 928\) cm⁻¹.
These values refer to matrix isolated WO₂ molecules at low temperatures (in neon and argon gas matrix 4 and 20 K) and have been obtained from analysis of electronic transition spectra with long vibrational progressions [14]. Vibrations in different WO₃ polymorphous phases occur in the same range [15]. Hence, WO₂²⁺ stretches and bendings should occur at about 1100, 900 and 390 cm⁻¹. For the melts, we observed (Table 2) the appearance of two of these bands, ν₁ = 1045 and ν₂ = 368 cm⁻¹, ν₃ being probably weak and broad. The higher values observed here relative to the WO₂ at low temperature are due to the hexavalent state of W in the [WO₂]²⁺ ion and to the high temperature.

This means, taking into consideration the low symmetry and the bonding between the WO₂²⁺ and SO₄²⁻ units in the dimeric
\[ \{\text{W}^{VI}\text{O}_2(\text{SO}_4)_2\}_{2}(\mu-\text{SO}_4)_2\}^8- \], that excessive mixing of group vibrations must occur. The assignments presented in Table 2 are therefore only tentative approximations.

In Fig. 8 we present Raman spectra of four \( K_8\{\text{W}^{VI}\text{O}_2(\cdot-\text{SO}_4)_2\}_{2}(\mu-\text{SO}_4)_2\} \) crystals, recorded while still inside the ampoule. The crystals were grown and decanted from a melt at \( \sim 600 \, ^\circ\text{C} \) of composition \( X = 0.27 \) (\( X \) = formal mole fraction of \( \text{WO}_3 \) in the \( \text{WO}_3-K_2\text{SO}_4-K_2\text{S}_2\text{O}_7 \) system).

Again stretching vibrations from \( \text{WO}_2^{2+} \) and \( \text{SO}_4^{2-} \) are assigned to bands between \( \sim 1100 \) and \( \sim 900 \, \text{cm}^{-1} \). We clearly see increasing bands that we assign to coordinated sulfate: bridging \( v_1(C_{2v}) \) at \( \sim 950 \, \text{cm}^{-1} \) and terminal \( v_1(C_{3v}) \) at \( \sim 925 \, \text{cm}^{-1} \). \( \text{WO}_2^{2+} \) bendings can be assigned to the bands in the range from \( \sim 200 \) to \( \sim 400 \, \text{cm}^{-1} \), as presented in Table 2.

The narrow lines seen below \( 150 \, \text{cm}^{-1} \) are rotational bands from the air surrounding the ampoule. Bands likely to be (at least partly) due to traces of the frozen \( \text{K}_2\text{S}_2\text{O}_7 \) solvent are indicated with asterisks in Fig. 8.

4. Conclusion

By means of Raman spectroscopy and X-rays work [8], it has been possible to determine and confirm the stoichiometry of the reactions as 1:1:1. We have only indication of formation of one kind of complex, the dimeric \( K_8\{\text{W}^{VI}\text{O}_2(\cdot-\text{SO}_4)_2\}_{2}(\mu-\text{SO}_4)_2\} \) with two bridging sulfate ligands and four terminally bound sulfato groups. The complex seems to be very stable and exists as the only compound formed in the molten and solid state. It seems reasonable to describe the system in terms of the formation of rather free bent \( \{\text{WO}_2\}^{2+} \) ions of \( C_{2v} \) point group symmetry with fundamentals at around: \( v_1 = 1045, \ v_2 = 278 \, \text{cm}^{-1} \), and with \( v_3 \) being weak and broad at the high temperature. In the dimeric \( \{\text{W}^{VI}\text{O}_2(\cdot-\text{SO}_4)_2\}_{2}(\mu-\text{SO}_4)_2\}^8- \) complexes, excessive mixing of these \( \{\text{WO}_2\}^{2+} \)-group vibrations with modes in coordinated bridging and terminal sulfate \( \{v_1(C_{2v})\} \) at \( \sim 950 \, \text{cm}^{-1} \) and \( v_1(C_{3v}) \) at \( \sim 925 \, \text{cm}^{-1} \) must occur so the assignments presented are only tentative approximations.

Acknowledgments

The authors acknowledge Bodil Holten and Lise Lotte Berring of the Technical University of Denmark for preparative and crystallographic help. I.M. Ferré thanks the Erasmus Program of the European Union for a studentship making the visit to Denmark possible.

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