Structure of Vanadium Oxosulfato Complexes in $V_2O_5-M_2S_2O_7-M_2SO_4$ (M = K, Cs) Melts. A High Temperature Spectroscopic Study

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The V^V and V^{IV} oxosulfato complexes formed in V₂O₅-M₂S₂O₇-M₂SO₄ (M = K, Cs) melts under SO₂(g) or O₂(g) atmosphere have been studied by electronic absorption (VIS/NIR) and Raman spectroscopy at 450 °C. VIS/NIR spectra have been obtained at 450 °C for V₂O₅-K₂S₂O₇ molten mixtures in SO₂ atmosphere ($P_{SO_2} = 0-1.2$ atm). The data are in agreement with the V^V \leftrightarrow V^{IV} equilibrium: (VO)₂O(SO₄)₄⁴⁻(1) + SO₂(g) \leftrightarrow 2VO(SO₄)₂²⁻(1) + SO₃(g). SO₂ does not coordinate to the V^V complex but starts significantly to coordinate to V^{IV} for $P_{SO_2} > 0.4$ atm according to VO(SO₄)₂²⁻(1) + SO₂(g) \leftrightarrow VO(SO₄)₂SO₂²⁻(1). The Raman spectral features and the exploitation of the relative Raman intensities indicate that the (VO)₂O(SO₄)₄⁴⁻ *dimeric* complex unit, possessing a V-O-V bridge, is formed in the V₂O₅-M₂S₂O₇ *binary* mixtures. The spectral changes occurring upon interaction of the binary V₂O₅-K₂S₂O₇ mixtures with SO₂ or addition of M₂SO₄ to the binary V₂O₅-M₂S₂O₇ mixtures indicate a cleavage of the V-O-V bridge and formation of the V^{IV}O(SO₄)₂²⁻ or V^VO₂(SO₄)₂³⁻ *monomeric* complex units, respectively. The most characteristic bands due to the various complexes in the melts have been assigned. The spectral data are discussed in terms of possible structures. For the first time, high-temperature vibrational spectroscopy has been used to study the structural and vibrational properties of V₂O₅-K₂S₂O₇ and V₂O₅-K₂S₂O₇-K₂S₂O₄ melts. The results are valuable for the mechanistic understanding of SO₂ oxidation at the molecular level.

Introduction

The catalyst used for sulfuric acid production, catalyzing the reaction $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$, is a supported liquid phase (SLP) catalyst, usually made by calcination of diatomaceous earth, V₂O₅ (or other V salts), and alkali salt promoters (usually in the form of their sulfates) with the alkali-to-vanadium ratio ranging from 2 to 5. During the activation process, the catalyst takes up SO₃, forming molten alkali pyrosulfates, which dissolve the vanadium salts.¹ Thus, the molten salt/gas system V_2O_5 - $M_2S_2O_7 - M_2SO_4/SO_2 - O_2 - SO_3 - N_2$ (M = K, Na, Cs or mixtures of these) at 400-600 °C is considered to be a realistic model of the working industrial catalyst. Recently, the catalyst has been used also for desulfurization of power plant flue gas.² Despite persistent research efforts, conclusions concerning the molecular structure of the V^V and especially V^{IV} complexes participating in the catalytic cycle are still lacking due to the difficulties encountered in spectroscopic studies of supported molten salt catalysts.³

So far, various methods including potentiometry, cryoscopy, spectrophotometry, conductometry, calorimetry, NMR, cyclic voltammetry, and Raman spectroscopy have been used to study the V^V complexes in V₂O₅ $-M_2S_2O_7-M_2SO_4$ (M = K, Cs) melts.^{4–11} The phase diagrams of the V₂O₅ $-M_2S_2O_7$ (M = 80% K + 20% Na),¹² V₂O₅ $-K_2S_2O_7$,¹³ V₂O₅ $-Cs_2S_2O_7$,¹⁴ and V₂O₅ $-Rb_2S_2O_7$ ¹⁵ systems have been constructed. The only V^V

compounds isolated from the $V_2O_5-M_2S_2O_7$ molten systems and characterized by single-crystal X-ray study are the Cs₄-(VO)₂O(SO₄)₄, 16 Rb₄(VO)₂O(SO₄)₄, 15,17 and K₄(VO)₂O(SO₄)₄. 13,17

The complex formation of V^{IV} and the equilibrium V^V \leftrightarrow V^{IV} in the molten salt–gas system V₂O₅–K₂S₂O₇/SO₂–SO₃–N₂ in controlled SO₂–SO₃ atmospheres have been studied by high-temperature VIS/NIR and ESR spectroscopy.³ The importance of the lower valence states of vanadium (V^{IV} and V^{III}) is well recognized, because precipitation of V^{IV} and V^{III} compounds has been shown to cause deactivation of catalyst melts.^{18,19}

In the present work, high-temperature VIS/NIR spectroscopy is applied to study the complex formation of V^V and V^{IV} in the molten salt–gas system V₂O₅–K₂S₂O₇/SO₂ at 450 °C in order to investigate the possible coordination of SO₂ to the V^V and V^{IV} complexes formed in the catalyst. The VIS/NIR study is limited to dilute solutions of V^{IV}, i.e., 0.5 mol/L (corresponding to $X_{V_{2}O_{5}} = 0.03$) due to the very high absorbance of the studied melts in the visible and UV regions. The composition of the industrial catalysts lies in the range of 3–4.5 mol V/L (corresponding to $X_{V_{2}O_{5}}$ in the range of 0.17–0.22) for the V₂O₅–K₂S₂O₇ binary system.

Furthermore, the present work is concerned with the structural and vibrational properties of (i) the V^V and V^{IV} oxosulfato complexes formed in binary V₂O₅-M₂S₂O₇ (M = K or Cs) melts under SO₂-O₂(g) atmosphere and (ii) the V^V oxosulfato complexes formed in the ternary V₂O₅-M₂S₂O₇-M₂SO₄ (M = K or Cs) melts under O₂(g) atmosphere. High-temperature Raman spectroscopy is applied at 450 °C and in the following V₂O₅ mole fraction ranges: (a) 0-0.25 for V₂O₅-K₂S₂O₇ (up

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Figure 1. Cell assembly connecting two rectangular optical cells (a) cell containing molten salt mixture and (b) cell used for measurements in the gas phase.

to 4.8 mol V/L), (b) 0-0.25 for V₂O₅-K₂S₂O₇-K₂SO₄, (c) 0-0.33 for V₂O₅-Cs₂S₂O₇ (up to 8.6 mol V/L), and (d) 0-0.25 for V₂O₅-Cs₂S₂O₇-Cs₂SO₄. Thus, the Raman study covers the very dark and viscous melts characteristic of the industrial catalyst.

Experimental Section

Chemicals and Sample Preparation. The hygroscopic $K_2S_2O_7$ and $Cs_2S_2O_7$ were made by thermal decomposition of K₂S₂O₈ (Merck p.a.) and Cs₂S₂O₈ (synthesized as discussed previously¹⁴). V_2O_5 (Cerac, pure 99.9%), K_2SO_4 (Fluka p.a), and Cs₂SO₄ (Alfa, 99.999%) were dried in vacuo at 300 °C for 4 h and stored in the glovebox until use. The gases used were SO₂ (Matheson, Union-Carbide, 99.98%), N₂ (L'Air Liquide, 99.999%), and O₂ (L'Air Liquide, 99.99%). All handling of the chemicals and filling of the VIS/NIR and Raman optical cells took place in a nitrogen filled glovebox. Preweighed amounts of the chemicals were transferred into clean, dry, flamed, and degassed optical cells. The cells were then attached to a gasaddition/vacuum line equipped with a mercury manometer for introducing the gases at the desired pressures. The VIS/NIR cell assembly (Figure 1) was then closed with a Teflon stopcock, whereas the Raman cells were immersed in liquid nitrogen for trapping the gases and were finally sealed under vacuum.

The symbol X_i^0 denotes the initial mole fraction of the components of the V₂O₅-M₂S₂O₇ binary mixture (weighed-in amounts). The composition of the V₂O₅-M₂S₂O₇-M₂SO₄ ternary mixture is defined by combining $X_{V_2O_5}^0$ (neglecting M₂-SO₄) with the ratio $n(SO_4^{2-})/n(V)$ of the number of sulfate groups added per mole of vanadium. This ratio was varied between 0 and 2.5.

Spectrophotometry. A cell assembly (Figure 1) connecting two rectangular fused-silica optical cells (Ultrasil from Helma, Germany) was used for the spectrophotometric study. An optical cell with a 0.2 cm path length was used for obtaining the VIS/ NIR spectra of the V^{IV} and V^V complexes in the melt. For determining the equilibrium partial pressure of SO₂ in the gas phase, optical cells with 0.05 or 0.2 cm path lengths were used (depending on the SO₂ pressure), and the absorbance at 300.2 nm was measured in the UV/vis spectrum of the gas. Appropriate linear P_{SO_2} vs $A_{300.2}$ calibration lines were constructed. The cell part containing the melt was mounted in an upright position inside an optical furnace, which was placed in the sample compartment of a Hitachi U-3000 spectrophotometer. A period of several days was necessary to equilibrate the $K_2S_2O_7-V_2O_5(1)/SO_2(g)$ mixtures at 450 °C, and progress toward equilibrium was followed by recording the spectrum of the molten phase and measuring the absorbance at 730 nm due to the V^{IV} complexes. After equilibrium in the melt was established, the partial pressure of SO₂ was found to decrease, and the spectrum of the gas phase was recorded for determining (i) the final equilibrium pressure of SO₂ and (ii) the number of SO₂ moles that were consumed.

The quantitative interpretation of the spectra is based on Beer's law. As explained previously,³ the redox equilibrium $V^V \Leftrightarrow V^{IV}$ involves only two absorbing species (one V^V and one V^{IV}), and the measured optical density, *A* (absorbance), is related to the concentration of the absorbing species according to

$$\frac{A}{l} = \epsilon_{\rm VV} c_{\rm VV} + \epsilon_{\rm VIV} c_{\rm VIV} \tag{1}$$

where *l* is the path length (cm), c_V^{ν} and $c_{V^{IV}}$ are the equilibrium concentrations of the V^V and V^{IV} species (mol/L), ϵ_V^{ν} and $\epsilon_{V^{IV}}$ are the molar absorptivities (L mol⁻¹ cm⁻¹) of the absorbing species, and $c_V^{\nu} + c_{V^{IV}} = c_V^0 (c_V^0 \text{ denotes the initial concentration of vanadium}). The values of <math>\epsilon_V^{\nu}$ and $\epsilon_{V^{IV}}$ determined previously^{3,20} are $\epsilon_V^{\nu} = 1.57 \pm 0.02 \text{ L mol}^{-1} \text{cm}^{-1}$ and $\epsilon_{V^{IV}} = 19.61 \pm 0.08 \text{ L mol}^{-1} \text{cm}^{-1}$ at 730 nm and 450 °C.

The decrease in the number of moles of SO_2 can be due to (i) reduction of V^V to V^{IV} ($^{1}/_2$ mol SO_2 needed per mol of vanadium) and (ii) possible coordination of SO_2 to V^V or to V^{IV} complexes. The solubility of SO_2 in molten $K_2S_2O_7$ is small and can be neglected.²¹ The number of moles of SO_2 coordinated to vanadium (V^V or V^{IV}), n_{SO}^c , is defined by the mole balance

$$n_{\rm SO_2}^{\rm c} = n_{\rm SO_2}^{\rm 0} - 1/2n_{\rm VIV} - n_{\rm SO_2}^{\rm eq}$$
(2)

where $n_{SO_2}^0$ is the number of moles of SO₂ initially added, $1/_{2}n_V^{IV}$ is the number of moles of SO₂ used for reducing vanadium, and $n_{SO_2}^{eq}$ is the number of moles of SO₂ in the gas phase at equilibrium. The densities of the V₂O₅-K₂S₂O₇ melts are taken from previous work,⁷ and the melt volume is assumed unchanged, regardless of the gas atmosphere applied.

Raman Spectroscopy. The Raman cells were made of cylindrical fused silica tubing $(4 \pm 0.1 \text{ mm o.d.}, 3 \pm 0.1 \text{ mm} \text{ i.d.}, \text{ and } \sim 3 \text{ cm}$ long for the part containing the melts). The spectra were excited with the 647.1 and 676.4 nm lines of a Spectra Physics Stabilite model 2017 krypton ion laser and the 514.5 nm line of a Spectra Physics model 164 argon ion laser. The scattered light was collected at an angle of 90°, analyzed with a 0.85 m Spex 1403 double monochromator, and detected with a -20 °C cooled RCA photomultiplier. The Raman optical furnace has been described previously.²²

A period of 5–8 days was needed to equilibrate the $K_2S_2O_7$ – $V_2O_5(1)/SO_2(g)$ mixtures at 450 °C due to slow diffusion of SO₂, whereas overnight heating at 450 °C was sufficient for equilibrating the $M_2S_2O_7-V_2O_5(1)/O_2(g)$ (M = K or Cs) mixtures. The $M_2S_2O_7-V_2O_5-M_2SO_4$ melts had to be heated for up to 20 days to attain equilibrium due to slow dissolution of the sulfate.

Obtaining Raman spectra at elevated temperatures for these very dark-colored, viscous, and hygroscopic melts was very difficult due to strong absorption of the laser light. Attempts to detect scattered light from the V^V containing melts using the 514.5, 488.0, and 457.0 nm argon lines as excitation sources failed. This is because a strong charge-transfer band occurs in the UV/vis spectra of $M_2S_2O_7-V_2O_5$ and $M_2S_2O_7-M_2SO_4-V_2O_5$ melts,^{5,23} and Raman spectra could only be obtained with



Figure 2. VIS/NIR spectra of the V₂O₅-K₂S₂O₇ mixture ($c_V^0 = 0.25$ mol V₂O₅/L) at 450 °C equilibrated with (a) $P_{O_2} = 0.2$ atm, (b) $P_{SO_2} = 0.08$ atm, (c) $P_{SO_2} = 0.20$ atm, (d) $P_{SO_2} = 0.25$ atm, and (e) $P_{SO_2} = 0.30$ atm.

the 647.1 and 676.4 nm krypton lines. Better results were obtained with the 647.1 nm line, which overlaps with the tail of the electronic charge-transfer band of V^V , and therefore, the obtained spectra are of preresonance character, leading to enhancement of the band intensities. In certain cases, light reflected from the walls of the quartz cells had to be masked by proper adjustment of the monochromator entrance slit height.

Results and Discussion

VIS/NIR Spectra of the V2O5-K2S2O7/SO2(g) System at 450 °C. The VIS/NIR spectra were recorded in the range of 550-900 nm at 450 °C for 0.25 mol/L V2O5 (i.e. 0.5 mol/L V) solutions in K₂S₂O₇ under 20 different SO₂ partial pressures in the range $0 < P_{SO_2} < 1.5$ atm. For convenience, only some of the spectra obtained are shown in Figure 2. The band at 730 nm (13 700 cm⁻¹) is due to V^{IV} complexes and is assigned to the Lapporte-forbidden $d-d^2B_2(d_{xy}) \rightarrow {}^2E(d_{xz}, d_{yz})$ electronic transition of V^{IV} in the distorted octahedral field of a complex of the vanadyl ion (VO²⁺) with equatorially coordinated bidentate SO₄ ligands in a C_{2v} configuration.³ The isosbestic point found at around 620 nm and 16 L mol⁻¹ cm⁻¹ compares well with the values found previously.^{3,23} A graphical summary of the results is shown in Figure 3, where for each experiment, the degree of vanadium reduction, $n_{\rm V}^{\rm IV}/n_{\rm V}$, and the coordination number, $n_{SO_2}^c/n_V$, i.e., the number of moles of SO₂ coordinated per mole of vanadium, are plotted against P_{SO_2} at equilibrium. The results show that SO₂ does not coordinate to V^V complexes (which are reduced to V^{IV} even at very low $P_{SO_2}^{eq}$) but only to V^{IV}, apparently at $P_{SO_2}^{eq} > 0.4$ atm, increasing to a coordination number of 1 at $P_{SO_2}^{eq} \approx 1.2$ atm. The scattering of the data in Figure 3 reflects the experimental difficulties. At $P_{SO_2}^{eq} \ge 1.4$ atm, precipitation of a crystalline compound was observed. The green (VIII) hexagonal crystals (isolated after cooling and flushing the solidified melt with water) were reminiscent of KV- $(SO_4)_2$, which is known to be one of the deactivation products



Figure 3. Plots of the degree of vanadium reduction, $n_{V^{IV}}/n_V$ (O), and of the coordination number, $n_{SO_2}^c/n_V$ (Δ), as a function of the partial pressure of SO₂, P_{SO_2} , at equilibrium.

TABLE 1: V^V↔V^{IV} Model Redox Equilibria^a

model No.	model equilibrium	equilibrium constant	σ	K/P _{SO3}
1	$(\mathbf{V}^{\mathrm{V})}_2 + \mathrm{SO}_2 \nleftrightarrow (\mathbf{V}^{\mathrm{IV}})_2 + \mathrm{SO}_3$	$K_{1} = \frac{c_{(\text{VIV})_{2}}}{c_{(\text{VV})_{2}}} \frac{P_{\text{SO}_{3}}}{P_{\text{SO}_{2}}}$	0.325	33.7
		$(c_{\rm VIV})^2 P_{\rm SO_3}$		

2
$$2V^{V} + SO_2 \leftrightarrow 2V^{IV} + SO_3$$
 $K_2 = \frac{(V_{1V})^2}{(c_{VV})^2} \frac{SO_3}{P_{SO_2}}$ 369.9 330

3
$$(V^{V})_{2} + SO_{2} \leftrightarrow 2V^{IV} + SO_{3}$$
 $K_{3} = \frac{(c_{VIV})^{2}}{(c_{VV})_{2}} \frac{P_{SO_{3}}}{P_{SO_{2}}}$ 0.239 29.3

4
$$2V^{V} + SO_{2} \leftrightarrow (V^{IV})_{2} + SO_{3}$$
 $K_{4} = \frac{c_{(V^{IV})_{2}}}{(c_{VV})^{2}} \frac{P_{SO_{3}}}{P_{SO_{2}}}$ 428.2 376

^{*a*} Equilibrium constants (K/P_{SO_3}) and variances (σ) at 450 °C.

of the sulfuric acid catalyst. 18,19 The powder IR and Raman spectra of these crystals were indeed the same as the known spectra of $KV(SO_4)_2.^{24}$

Previous studies^{5–9} suggest that, in dilute $V_2O_5-K_2S_2O_7$ molten solutions, V^V is present in the form of monomeric or dimeric complexes and V^{IV} presumably behaves in a similar way. The possible combinations of these proposed complexes give rise to four model equilibria, which are presented in Table 1.

Now, for each measurement, the partial pressure of SO₂ is known, and by using eq 1 and the ϵ_V^v and $\epsilon_{V^{IV}}$ values, the concentrations of the vanadium species participating in the four model redox equilibria can be calculated. The partial pressure of SO₃ above the dilute V₂O₅-K₂S₂O₇ mixtures studied is unknown but presumably constant, i.e., equal to the partial pressure of SO₃ over molten K₂S₂O₇ at 450 °C. Therefore, the relation between P_{SO_2} and the appropriate concentration quotient for the correct model using the 7 different measurements in the range 0 < P_{SO_2} < 0.4 atm, i.e., before SO₂ starts to coordinate significantly to the V^{IV} complex, should be linear with a slope corresponding to P_{SO_3}/K . The variances given in Table 1 are the results of least-squares fits of the concentration quotient for each particular model vs the partial pressure of SO_2 and suggest the exclusion of models 2 and 4. This result combined with the ESR evidence^{3,23} for *monomeric* V^{IV} complexes in the studied melts, a fact which excludes model 1, points to model 3 as the most plausible model. Thus, the redox equilibrium could be formulated as

$$(VO)_2O(SO_4)_4^{4-}(1) + SO_2(g) \leftrightarrow 2VO(SO_4)_2^{2-}(1) + SO_3(g)$$
(3)
$$P_{SO_3}/K = 29.3 \text{ L mol}^{-1} \text{atm}^{-1}$$

The above complex formulas are deduced from previous knowledge of the complex chemistry of vanadium in pyrosulfate melts^{3-9,11} and are in agreement with a recent potentiometric and ESR study.²³ The results from the Raman study discussed below confirm that the V^V and V^{IV} complexes shown in (3) are indeed the most plausible ones. Moreover, the equilibrium constant of reaction 3 has previously been determined: $K = 0.0145 \text{ L mol}^{-1}$ at 450 °C.³ Thus, by taking into account the above P_{SO_3}/K value, one can calculate the equilibrium partial pressure of SO₃ over the V₂O₅-K₂S₂O₇ melt studied at 450 °C as $P_{SO_3} = (4.9 \pm 0.3) \times 10^{-4}$ atm.

Finally, the coordination of SO_2 to the V^{IV} complex assuming a SO_2 coordination number of 1 (according to the results shown in Figure 3) could be formulated as

$$\operatorname{VO}(\operatorname{SO}_4)_2^{2^-}(l) + \operatorname{SO}_2(g) \nleftrightarrow \operatorname{VO}(\operatorname{SO}_4)_2 \operatorname{SO}_2^{2^-}(l) \quad (4)$$

Note that in the previous study of the $V_2O_5-K_2S_2O_7$ system at equilibrium in controlled SO_2/SO_3 atmospheres³ it was not possible to exclude model 2, which however could be excluded in the present study.

Raman Spectra of the V₂O₅–M₂S₂O₇/O₂(g) Systems (M = K or Cs). Several V₂O₅–M₂S₂O₇ mixtures with $X_{V_2O_5}^0 =$ 0–0.25 for the K system and $X_{V_2O_5}^0 =$ 0–0.33 for the Cs system were placed in cells which were then sealed under oxygen ($P_{O_2} = 0.2$ atm) in order to stabilize vanadium in the +5 state. By dissolution of V₂O₅ in M₂S₂O₇ (M = K or Cs) at 450 °C, dark brown melts were obtained, the colors of which were much darker for the K containing melts. Therefore, Raman spectra could not be obtained for the K melts at $X_{V_2O_5}^0 > 0.25$, because of very strong absorption of the excitation laser lines used. However, spectra obtained from the two systems were similar.

Figure 4 shows Raman spectra obtained from $V_2O_5-K_2S_2O_7$ molten mixtures at nine different compositions. The Raman spectra of molten $K_2S_2O_7$ are included in Figure 4 for comparison. Addition of V_2O_5 gives rise to the appearance of new bands the assignments and polarization characteristics of which are summarized in Table 2. The most prominent among these bands, which are attributed to the V^V complex formed, are observed at 1050, 1000, 830, 780, 676, and 392 cm⁻¹. The intensities of these bands increase relative to the bands of $S_2O_7^{2-}$ with increasing amounts of V_2O_5 added and dominate the spectrum of the sample with $X_{V_2O_5}^0 = 0.25$, indicating that the reaction taking place leads to a vanadium oxosulfato complex at the expense of $S_2O_7^{2-}$. Table 2 lists also the Raman bands, polarization characteristics, and assignments for the $V_2O_5 Cs_2S_2O_7$ melts, of which the spectra are similar to those shown in Figure 4. The stoichiometry of the reaction



Figure 4. Raman spectra of the V₂O₅-K₂S₂O₇ molten mixtures at 450 °C in oxygen atmosphere ($P_{O_2} = 0.2$ atm) (a) $X_{V_2O_5}^0 = 0$, (b) $X_{V_2O_5}^0 = 0.03$, (c) $X_{V_2O_5}^0 = 0.054$, (d) $X_{V_2O_5}^0 = 0.063$, (e) $X_{V_2O_5}^0 = 0.087$, (f) $X_{V_2O_5}^0 = 0.100$, (g) $X_{V_2O_5}^0 = 0.150$, (h) $X_{V_2O_5}^0 = 0.200$, (i) $X_{V_2O_5}^0 = 0.228$, and (j) $X_{V_2O_5}^0 = 0.249$. Spectral conditions: $\lambda_0 = 647.1$ nm; laser power, 175 mW; scan speed, 60 cm⁻¹ min⁻¹ (a-g), 18 cm⁻¹ min⁻¹ (h-j); time constant, 0.3 s (a), 1 s (b-d), 3s (e-j); spectral slit width, 6 cm⁻¹.

where C denotes the complex, can be determined by exploiting the relative Raman band intensities of the spectra, shown in Figure 4, by a recently derived method based on the definition of the following parameters, I^* and I° :²⁵

$$I^{*} = \frac{(I_{S_{2}O_{7}^{2-},1085})/X_{S_{2}O_{7}^{2-}}^{0}}{(I_{\text{complex},1050})/X_{V_{2}O_{5}}^{0}}$$
(6)

$$I^{\circ} = \frac{\langle v_{S_2O_7^{-2^-},1085} / v_{eq,S_2O_7^{-2^-}}}{(I_{\text{complex},1050}) / N_{eq,\text{complex}}}$$
(7)

*I** is plotted vs $X_{V_2O_5}^0$ in Figure 5a and extrapolates to 0.36 pointing to a stoichiometry near 1:2 (n = 2).

 I° is plotted vs $X_{V_2O_5}^0$ in Figure 5b for different assumed values of *n*. The numerator and denominator of eq 7 should each be independent of $X_{V_2O_5}^0$; the scattering power per molecule of $S_2O_7^{2-}$ (numerator) or complex ion (denominator) are universal *constants*, apart from an instrumental factor which cancels in eq 7. The number of moles at equilibrium for each species, $N_{eq,i}$, can be calculated by assuming a value for *n* in reaction 5 and considering the appropriate mass balances.²⁵ From Figure 5b, we conclude that n = 2, leading to a constant value for I° . Thus

$$V_2O_5 + 2S_2O_7^{2-} \rightarrow (VO)_2O(SO_4)_4^{4-}(l)$$
 (8)

in accordance with eq 3 and the previous evidence for the dimeric V(V) complex mentioned above. The following discus-

TABLE 2: Raman Frequencies (cm⁻¹) for $V_2O_5 - M_2S_2O_7/O_2(g)$, $V_2O_5 - M_2S_2O_7 - M_2SO_4/O_2(g)$, and $V_2O_5 - K_2S_2O_7/SO_2(g)$ Molten Mixtures at 450 °C (M = K or Cs)^{*a*}

$V_2O_5-M_2S_2O_7/O_2(g)$			$V_2O_5-M_2S_2O_7-M_2SO_4/O_2(g)$			$V_2O_5 - K_2S_2O_7/SO_2(g)$	
M = K	M = Cs	assignments for $(V^VO)_2O(SO_4)_4^{4-}$	M = K	M = Cs	assignments for $V^VO_2(SO_4)_2^{3-}$	M = K	assignments for V ^{IV} O(SO ₄) ₂ SO ₂ ²⁻
1180 m,p	1175 m,p	$\nu_3(SO_4)$	1168 w	1166 w	$\nu_3(SO_4)$	1170 w,p 1135 w,p	$ \nu_3(SO_4) $ $ \nu_s(SO_2) $
1050 s,p	1046 s,p	ν(V=O)	1042 s,p 968 ^b s,p	1037 s,p 961 ^b s,p	ν (V=O) ν_1 of free SO ₄ ²⁻	1038 m,p	ν(V=O)
1000 m,p	996 m,p	$\nu(S-O_{terminal})$	940 s,p	938 s,p	$\nu(S-O_{terminal})$	990 w,sh,p 965 m,p	$\nu(S-O_{terminal})$
830 s,br,p	825 s,br,p	$\nu(S-O_{bridging})$	~880 sh,br,p ~825 br	\sim 880 sh,br,p	$\nu(S-O_{bridging})$	935 m,sh,p	$\nu(S-O_{bridging})$
770 m,p	765 m,p 690 w,p	ν (V-O-V)	668 m,p	665 m,p		ر 686 m,p	$\nu_4(\mathrm{SO}_4)$
676 w,p 608 w,p	669 w,p 611 w,p	$\nu_4(\mathrm{SO}_4)$	618 vw,dp 600 w,dp	611 w,dp 598 w,dp	$\nu_4(SO_4)$	~600 w,dp }	ν (V-O _{equat})
586 m,p 488 m,p	582 m,p 483 m,p	ν (V-O _{equat})	534 w,p 486 w,p	533 w,p 485 w,p	ν (V-O _{equat})		
392 dp 305 s,p	390 dp 302 s,p	$\nu_2(\mathrm{SO}_4)$	408 s,p 282 sh,dp	406 s,p 279 sh,dp	$\nu_2(SO_4)$		
195 sh, p	194 sh,p	$\nu[(O=V)-O_{tr}]$	228 s,dp	227 s,dp	$\nu[(O=V)-O_{tr}]$		

^{*a*} Abbreviations: s = strong; m = medium; w = weak; br = broad; sh = shoulder; v = very; p = polarized; dp = depolarized. ^{*b*} Seen in melts saturated with M₂SO₄.



Figure 5. (a) Plot of I^* vs $X^0_{V_2O_5}$. An approximate value of n = 2 is found, corresponding to crossing at 0.33; (b) plot of I° vs $X^0_{V_2O_5}$ for various values of n. A value of n = 2 is found.

sion on band assignments and the results from the Raman study of the $V_2O_5-M_2S_2O_7-M_2SO_4$ molten mixtures supports this interpretation.

One should expect to observe the group vibrations of VO³⁺ and SO₄²⁻ units of the (VO)₂O(SO₄)₄⁴⁻ dimer V^V complex formed according to reaction 8. The four sulfate fundamentals $(\nu_1 - \nu_4)$ for a tetrahedral T_d configuration span the following representation:

$$\Gamma_{\rm vib} = A_1(\nu_1) + E(\nu_2) + 2F_2(\nu_3 + \nu_4)$$

and are well-known²⁶ from Raman work on aqueous solutions: $\nu_1(A_1) \approx 980 \text{ cm}^{-1}$, $\nu_2(E) \approx 450 \text{ cm}^{-1}$, $\nu_3(F_2) \approx 1100 \text{ cm}^{-1}$, and $\nu_4(F_2) \approx 615 \text{ cm}^{-1}$. However, coordination of the sulfate ion and interactions with other ions are expected to shift the bands, reduce the symmetry, and lift the degeneracies of the ν_2 , ν_3 , and ν_4 modes. This behavior has already been observed in the Raman spectra of molten M₂SO₄-V₂O₅ (M = K or Cs) mixtures.²⁷

Within $Cs_4(VO)_2O(SO_4)_4$, there are four crystallographically different bidentate chelating SO₄ groups with greatly different

S-O distances¹⁶ and the structures of the K and Rb salts are similar.^{13,15,17} The S–O bonds involving oxygen not coordinated to vanadium (terminal S-O bonds) are in the range 1.43-1.44 Å, whereas the S-O bonds involving oxygen coordinated to vanadium (bridging S–O bonds) are unusually long (in the range 1.52-1.58 Å) far from the usual value of 1.47 Å found for sulfate groups. Furthermore, values of 968 and 961 cm⁻¹ are found for the $\nu_1(SO_4^{2-})$ mode of free sulfate in K₂S₂O₇ and $Cs_2S_2O_7$ melts, respectively (see Table 2 and Figure 6). It is therefore evident that if the $(VO)_2O(SO_4)_4^{4-}$ ion is the dimer complex formed in the melts then one shouldbe able to observe at least two bands due to S-O modes in the Raman spectra accounting for terminal and bridging S-O modes, which relative to the above value of 968 and 961 cm⁻¹ found for $\nu_1(SO_4^{2-})$, should lie at higher and lower wavenumbers, respectively. Thus, the band at 1000 cm^{-1} in the K containing melts in Figure 4 (seen at 996 cm^{-1} in the Cs melts) is assigned to terminal S–O stretching, whereas the broad band centered at 830 cm⁻¹ (seen at 825 cm^{-1} in the Cs melts) is assigned to bridging S–O modes. A large number of related configurations of bridging oxygen can account for the broadness of the latter band. This variation in S-O stretching frequencies is similar to that observed in Raman spectra of VO₂SO₄⁻ and VO₂(SO₄)₂³⁻ complexes in molten $M_2SO_4 - V_2O_5$ (M = K or Cs) mixtures²⁷ and is analogous to the differences observed between terminal and bridging metal-halogen stretching frequencies.²⁶ Moreover, the band at 1180 and several bands in the 400-680 cm⁻¹ range are assigned to split components of the $\nu_2 - \nu_4$ fundamentals of coordinated SO₄ ligands, and similar assignments are made for the Cs melts (see Table 2).

Turning our attention to V–O stretching modes and assuming octahedral coordination around V within $(VO)_2O(SO_4)_4^{4-}$ (as in the crystalline $Cs_4(VO)_2O(SO_4)_4^{16}$), we assign the 1050 cm⁻¹ band to the V^V=O terminal mode²⁶ and the 770 cm⁻¹ band to V–O–V bridging. Indeed, according to an empirical correlation between V–O stretching frequencies and bond lengths,²⁸ a value of 765 cm⁻¹ (found in the Cs melts, see Table 2) corresponds to a bond length of ca.1.74 Å, which is very close to the reported value of 1.77 Å for V–O bond lengths along the V–O–V bridge in crystalline $Cs_4(VO)_2O(SO_4)_4$.¹⁶ The discussion of the Raman spectra of the V₂O₅–M₂S₂O₇–M₂SO₄ melt, where cleavage of the V–O–V bridge caused by alterations in sulfate



Figure 6. Titration-like series of Raman spectra of the V₂O₅-Cs₂S₂O₇-Cs₂SO₄ molten mixtures ($X_{0205}^0 = 0.066$) at 450 °C in oxygen atmosphere ($P_{O2} = 0.2$ atm). Spectral conditions: $\lambda_0 = 647.1$ nm; laser power, 175 mW; scan speed, 60 cm⁻¹ min⁻¹; time constant, 0.3 s (a); spectral slit width, 6 cm⁻¹.

coordination leads to elimination of this band, will provide further confirmation to this assignment. The 586 and 488 cm⁻¹ bands are assigned to V–O modes along V–O–S chains in the equatorial plane of the VO₆ octahedra, in agreement with the relative V–O distances along the V–O–S chains of Cs₄-(VO)₂O(SO₄)₄¹⁶ and with the empirical correlation between V–O Raman stretching frequencies and bond lengths.²⁸ Similar assignments are done for the respective bands observed in the Cs melts.

Raman Spectra of the V₂O₅-M₂S₂O₇-M₂SO₄/O₂(g) Systems ($\mathbf{M} = \mathbf{K}$ or Cs). Addition of M₂SO₄ to the V₂O₅-M₂S₂O₇ melts results, as judged from the Raman spectra, in a reaction leading to alterations in SO₄ coordination and in the structure of the V^V complexes. The reaction was followed by recording Raman spectra for $V_2O_5-M_2S_2O_7$ samples with fixed $X_{V_2O_5}^0$ in which various amounts of M2SO4 were added. A careful study of the titration-like series of Raman spectra obtained (shown in Figure 6 for the V_2O_5 - $Cs_2S_2O_7$ - Cs_2SO_4 system with $X_{V_2O_5}^0$ = 0.066) shows that the $(VO)_2O(SO_4)_4^{4-}$ dimer reacts with the added sulfate up to a SO42-/VV ratio (ratio of number of added SO₄ moles vs the number of extant V^V atoms, denoted by Y in Figure 6) equal to 1. Actually, the spectra remain unchanged beyond Y = 1.40, and the extra 0.4 SO₄ ions per vanadium above Y = 1 correspond to the solubility of Cs_2SO_4 in molten $Cs_2S_2O_7$ ⁸ and the 961 cm⁻¹ band, seen for $Y \ge 1.40$, is due to the $\nu_1(A_1)$ mode of free dissolved SO₄²⁻. Excess Cs₂SO₄ added above Y = 1.40 remains as a precipitate. The dependence of Raman spectra for V2O5-Cs2S2O7 melts saturated with Cs2- SO_4 on the V_2O_5 content is shown in Figure 7a-c. The band at 938 cm⁻¹ is due to coordinated SO₄ and its relative intensity increases with increasing V₂O₅ content. Similar results are obtained for the V2O5-K2S2O7-K2SO4 system. The changes observed upon addition of sulfate (i.e., with increasing values of Y in Figure 6) are associated with the disappearance of the



Figure 7. (a–c) Raman spectra of the V₂O₅–Cs₂S₂O₇ molten mixtures saturated with Cs₂SO₄ at 450 °C in oxygen atmosphere ($P_{O_2} = 0.2$ atm); (a) $X_{V_2O_5}^0 = 0.027$, (b) $X_{V_3O_5}^0 = 0.066$, (c) $X_{V_2O_5}^0 = 0.147$. (d) Raman spectra of molten Cs₄(VO)₂O(SO₄)₄ saturated with Cs₂SO₄. (e) Raman spectra of the V₂O₅•Cs₂S₂O₇•2Cs₂SO₄ molten mixture. Spectral conditions: $\lambda_0 = 647.1$ nm; laser power, 175 mW; scan speed, 60 cm⁻¹ min⁻¹; time constant, 0.3 s; spectral slit width, 6 cm⁻¹.

996 (S–O_{terminal}), 825 (S–O_{bridging}), and 765 (V–O–V) cm⁻¹ bands and the appearance of the 938/961 cm⁻¹ doublet. Thus, sulfate addition results in cleavage of the V–O–V bridge and in formation of a V^V complex with sulfate ligands exhibiting much less distortion as judged from the relative departure of the 938 cm⁻¹ band from the 961 cm⁻¹ "ideal" value.

To examine the reaction of molten $Cs_4(VO)_2O(SO_4)_4$ with Cs_2SO_4 , the following procedure was adopted. $Cs_4(VO)_2O(SO_4)_4$ was synthesized by slow cooling of a $V_2O_5-Cs_2S_2O_7$ melt with $X_{V_2O_5}^0 = 0.33$ of which the Raman spectrum at 450 °C showed no bands due to $S_2O_7^{2-}$, indicating that the reaction was completed. This compound was then mixed with excess Cs_2 -SO₄ and equilibrated at 450 °C. The Raman spectrum of the resulting melt (Figure 7d) shows that the reaction proceeds with the formation of $S_2O_7^{2-}$ as indicated by the appearance of the characteristic 1078, 725, and 313 cm⁻¹ pyrosulfate bands. The above observations of the (i) 1:1 SO_4^{2-}/V^V ratio of the number of added SO_4 moles reacting vs number of extant V^V atoms and (ii) cleavage of the V–O–V bridge and production of $S_2O_7^{2-}$ upon sulfate addition can be accounted for by the following reaction scheme *only*:

$$(VO)_2 O(SO_4)_4^{4-} + 2SO_4^{2-} \rightarrow 2VO_2 (SO_4)_2^{3-} + S_2O_7^{2-}$$
(9)

Reactions 8 and 9 indicate that if all of the conclusions reached and the hypotheses made up to this point are correct then the constituents of $V_2O_5 \cdot M_2S_2O_7 \cdot 2M_2SO_4$ molten mixtures would react at 450 °C stoichiometrically to produce molten M_3VO_2 -(SO₄)₂ without leaving excess SO₄ or S₂O₇ ions. This is indeed the case as shown for the Cs system in Figure 7e depicting the Raman spectrum of the Cs₃VO₂(SO₄)₂ molten complex which is formed according to the following reaction: Structure of Vanadium Oxosulfato Complexes

$$V_2O_5 + S_2O_7^{2-} + 2SO_4^{2-} \rightarrow 2VO_2(SO_4)_2^{3-}$$
 (10)

which is merely a combination of reactions 8 and 9.

Raman Spectra of the V₂O₅–K₂S₂O₇/SO₂(g) System. To gain insight into the structural properties of the V^{IV} complexes, Raman spectra for oxidized and reduced samples of the same initial composition were obtained at 450 °C. Figure 8a shows Raman spectra for a 0.25 mol V₂O₅/L (i.e., $X_{V_2O_5}^0 = 0.03$) solution in K₂S₂O₇ under oxygen ($P_{O_2} = 0.2$ atm). Figure 8b shows spectra recorded for the same melt which has been equilibrated under SO₂ ($P_{SO_2} = 0.8$ atm) for 20 days, and its color has gradually turned from dark brown (characteristic of V^V) to dark green (characteristic for high content of V^{IV}). The Raman spectra of molten K₂S₂O₇ are also included in Figure 8c.

The Raman spectrum of the reduced melt shown in Figure 8b exhibits new (i.e., other than due to $S_2O_7^{2-}$) bands at ~600, 686, 935, 965, 990, 1038, 1135, and 1170 cm⁻¹ (see Table 2 for polarization characteristics and assignments). It is evident from Figure 3 that, for $P_{SO_2} = 0.8$ atm, vanadium is almost completely reduced from V^V to V^{IV} and furthermore that SO₂ is partly coordinated to the V^{IV} complex formed. A comparison between spectra in Figure 8a of the oxidized (V^V) melt and those of Figure 8b of the reduced (VIV) melt indicates a drastic change of the structural properties of the complexes involved. The bands at 830 and 1000 cm⁻¹ in spectrum a of Figure 8, which are due to bridging and terminal S-O stretches, are replaced by a triplet feature centered at 965 cm⁻¹ with shoulders at 935 and 990 cm^{-1} in spectrum b of Figure 8, thus indicating a much lower distortion of SO₄ ligands participating in the V^{IV} complex. Furthermore the 770 cm^{-1} band due to V–O–V bridging of the $(VO)_2O(SO_4)_4^{4-}$ dimer V^V complex is no longer present, indicating that the VIV complex formed is monomeric in agreement with the results of the VIS/NIR study.

The SO_4 modes of the V^{IV} complexes (Figure 8b) are identified at 600 and 686 (ν_4 split components), 935 (bridging S-O stretch along S-O-V chain), 965 (terminal S-O stretch), and 1170 cm⁻¹ (ν_3). The V^{IV}=O stretching is expected at 985 \pm 50 cm⁻¹.^{25,29} One could assign to V^{IV}=O stretching either the 965 or the 1038 cm⁻¹ band. These two bands correspond according to the V-O stretching frequency vs bond length correlation to V–O distances of 1.61 and 1.58 Å, respectively.²⁸ Significantly, the V-O distances between vanadium and the short bonded oxygen in the apical direction within VO_6 octahedra reported for VIV oxosulfato compounds isolated from $V_2O_5 - M_2S_2O_7$ (M = Na or K) melts are in the range 1.580-1.598 Å.^{30–32} Therefore, it is likely that the 1038 cm^{-1} band is due to V^{IV}=O stretching and the 965 cm⁻¹ due to terminal S-O stretch. Finally, the weak band at 1135 cm⁻¹ can be assigned to the symmetric stretching mode of SO2 coordinated to the V^{IV} through an oxygen atom,²⁶ probably trans to the shortbonded apical vanadyl oxygen of the $VO(SO_4)_2SO_2^{2-}$ complex formed according to reaction 4. Such a configuration is found also in crystalline VOSO₄SO₂-type compounds isolated from catalyst melts of relevant composition.¹⁹

Structural Models. The preceding discussion has revealed that the complex units formed are (i) the V^V dimer (VO)₂O-(SO₄)₄⁴⁻ in V₂O₅-M₂S₂O₇ (M = K, Cs) melts, (ii) the V^{IV} monomers VO(SO₄)₂²⁻ and VO(SO₄)₂SO₂²⁻ in V₂O₅-K₂S₂O₇ melts under SO₂ atmosphere, and (iii) the V^V monomer VO₂(SO₄)₂³⁻ in V₂O₅-M₂S₂O₇-M₂SO₄ (M = K, Cs) melts under O₂ atmosphere. These units do not occur necessarily in isolated "free" form but may participate in oligomeric or polymeric chainlike complex ions. This is pronounced in melts



Figure 8. Raman spectra of the molten mixture $K_2S_2O_7 - V_2O_5$ ($c_0 = 0.25 \text{ mol } dm^{-3} V_2O_5$) at 450 °C equilibrated under partial $P_{SO_2} = 0.2$ atm (a) and $P_{SO_2} = 0.8$ atm (b). The spectrum of the pure molten $K_2S_2O_7$ at 450 °C is included for comparison (c). Spectral conditions: $\lambda_0 = 647.1 \text{ nm}$ (a and c), 514.5 nm (b); laser power, 175 mW (a and c), 160 mW (b); scan speed, 60 cm⁻¹ min⁻¹ (a and c), 90 cm⁻¹ min⁻¹ (b); time constant, 1 s; spectral slit width, 6 cm⁻¹.



Figure 9. Possible structural models for (a) $(V^VO)_2O(SO_4)_4^{4-}$, (b) $V^VO_2(SO_4)_2^{3-}$ in monomeric and polymeric form, and (c) $V^{IV}O(SO_4)_2^{2-}$ and $V^{IV}O(SO_4)_2SO_2^{2-}$.

with high V_2O_5 content, whereby the viscosity and the glassforming ability of the melts increases, pointing to the existence of chainlike or network-like groups of ions.

Figure 9 depicts the possible structures of the abovementioned vanadium oxosulfato complexes. $(VO)_2O(SO_4)_4^{4-}$ is shown in Figure 9a with the same configuration found for the $M_4(VO)_2O(SO_4)_4$ (M = Cs, K, Rb) compounds.^{16,17} The structural models for the V^{IV} complexes are shown in Figure 9c. $VO(SO_4)_2^{2-}$ can be formulated from the vanadyl ion, VO^{2+} , and two bidentate chelating sulfate groups, giving rise to an apparent 5-fold coordination for vanadium. However, it is likely that one of the terminal sulfate oxygens lies trans to the vanadyl oxygen (in loose contact) by satisfying partly the preferential 6-fold coordination for vanadium. SO₂ may coordinate in this oxygen-deficient site through an O atom leading to VO(SO₄)₂SO₂²⁻ as shown in Figure 9c. Figure 9b shows the structural model for the VO₂(SO₄)₂³⁻ complex, formulated from the dioxovandium ion and two bidentate chelating SO₄ groups. Figure 9b shows also, as an example, an oligomeric chain consisting of this unit, in which VO₂SO₄⁻ units are linked by bidentate bridging SO₄ groups and the six-coordinated vanadium is found in the usual octahedral environment.

Conclusions

The combination of VIS/NIR and Raman spectroscopic investigations at 450 °C show that a redox equilibrium between *dimeric* V^V, (VO)₂O(SO₄)₄⁴⁻, and *monomeric* V^{IV}, VO(SO₄)₂²⁻, is established in V₂O₅-K₂S₂O₇/SO₂(g) melts. A quantitative treatment of the Raman band intensities *and* the Raman spectral features obtained from V₂O₅-M₂S₂O₇/O₂(g) (M = K or Cs) point to (VO)₂O(SO₄)₄⁴⁻ as the V^V complex formed. Bands due to V=O, V-O-V, and coordinated SO₄ groups were observed and assigned in the Raman spectra. The study covers the composition of industrial SO₂ oxidation catalysts used for sulfuric acid production and SO₂ removal from flue gases. Thus, it can be concluded that the active molten phase of these catalysts is dominated by the (VO)₂O(SO₄)₄⁴⁻ complex.

The VIS/NIR results show that the V^V complex, (VO)₂O-(SO₄)₄⁴⁻, does not coordinate SO₂ under the studied conditions but is reduced to monomeric VIV. It seems therefore likely that, as discussed recently,⁴ O₂ and not SO₂ is activated in the coordination sphere of the dimeric V^V complex prior to reaction with SO₂ as the initial step of the catalytic cycle for the reaction $2SO_2 + O_2 \rightarrow 2SO_3$. The proposed catalytic cycle⁴ involves only V^V species (dimeric or binuclear fragments of larger oligomers). The bidentate sulfate ligands found within the dimeric (VO)₂O(SO₄)₄⁴⁻ complex, Figure 9a, are strained due to their unusually large distortion and some of them may open up, making the complex coordinatively unsaturated in the horizontal positions and leading to the suggested coordination of O₂ as the first step of the catalytic cycle $[(VO)_2O(SO_4)_4^{4-} +$ $O_2 \leftrightarrow (VO)_2 O(SO_4)_4 O_2^{4-}]^4$ Coordination of SO₂ to form the monomeric V^{IV} complex, VO(SO₄)₂SO₂²⁻, is only important at rather high partial pressures of SO₂, much above the usual range for industrial SO₂ oxidation. The changes in the Raman spectra upon interaction of V₂O₅-K₂S₂O₇ with SO₂ or upon addition of M₂SO₄ to V₂O₅-M₂S₂O₇ mixtures point to cleavage of the V–O–V bridge and formation of the $V^{IV}O(SO_4)_2^{2-}$ or V^VO₂(SO₄)₂³⁻ monomeric complexes, respectively. Significant presence of sulfate can be encountered in industrial catalysts under certain conditions (e.g., at the inlet to the first bed where the high temperature, exceeding sometimes 600 °C, and the low conversion of SO₂ may shift the equilibrium $SO_4^{2-} + SO_3 \leftrightarrow$ $S_2O_7^{2-}$ to the left). The reported structural properties of the vanadium oxosulfato complexes are very useful for understanding the mechanism of the SO₂ oxidation at the molecular level.

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