TABLE II: Yield per Incident Energy ( $Y_{\rm E}$ ) at 1450 eV Relative to Regime II Plateau

thickness, nm	SO <sub>2</sub>		C <sub>4</sub> H <sub>8</sub>	
	EI	CI	EI	CI
41	0.18	0.34	0.05	0.08
61	0.17	0.40	0.03	0.07
78	0.21	0.21	0.07	0.05

N and Z are the number density and atomic numbers of atoms in the solid, e is the base of natural logarithm, and I is the mean excitation energy for electrons in the solid. Two quoted values for I in organic polymers are<sup>27,28</sup> 65 and 91 eV; these values predict dE/dx at E = 1450 eV to be reduced to 0.33 and 0.40 times the maximum, respectively. Experimentally observed ratios of SO<sub>2</sub> yields per unit incident energy at 1450 eV compared to the regime II plateau on three different film thicknesses with both ionization

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methods are listed in Table II. They appear to favor the diffusion length model; a more straightforward choice between the models could be based on their temperature dependence. This as well as a rationalization of the prominent decrease in the butene/SO<sub>2</sub> yields at high E must await further experiments.

#### Summary

The efficiency of the electron impact depolymerization reaction of thin films of poly(butene-1 sulfone) was measured with FTMS. Electrons with energy lower than the first allowed optical transition are effective in initiating the reaction. In the 20-200-eV energy range the G value for monomers is an order of magnitude higher than the reported values for bulk radiolysis; direct observation in the thin film geometry of products of reactions ascribed to secondary electrons in radiation chemistry allows to some extent the separation of effects of slow rate of escape in the solid phase. The use of FTMS as a means of detection provides sufficient sensitivity to measure volatile product yields at electron doses corresponding to energy deposition of less than 0.1  $\mu$ J.

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# IR Matrix Isolation Study of Alkali-Metal Metavanadate Monomers and Dimers

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In this paper are reported the results of matrix-isolation IR studies of lithium, sodium, potassium, and rubidium metavanadates. A critical analysis of these results in comparison with those of previous studies on the cesium metavanadate allows one to assume the existence of stable gaseous XVO<sub>3</sub> monomer and dimer species, both of importance in the equilibrium vapors, as definitely proved for X = K, Rb, and Cs, while reasonably inferred for X = Li and Na. Moreover, a  $C_{2v}$  symmetry can be reasonably assumed for the dimeric species. Mixed gaseous dimers with different alkali-metal atoms in their frame, like KCs(VO<sub>3</sub>)<sub>2</sub> and RbCs(VO<sub>3</sub>)<sub>2</sub>, have been also, for the first time, identified.

## Introduction

Alkali-metal metavanadates represent an outstanding problem in designing hot corrosion resistant ceramics. Indeed, thin films of these compounds (particularly  $NaVO_3$ ) or of their solutions in other fused salts, which can be formed in the operating conditions of a gas turbine and other critical high-temperature devices, are highly corrosive not only toward metals and alloys but also toward many oxides important for ceramic coatings and components. However, in spite of the increasing interest in their thermodynamic properties and chemical stability in different environments, alkali-metal metavanadates have been extensively studied only in solution where it is known they occur as trimeric and/or tetrameric aggregates.<sup>1,2</sup>

The literature available on their vaporization behavior, instead, is poor and even the vapor's composition is still controversial. Indeed, the first analysis of the vaporization gaseous products seems to be an infrared and Raman study of matrix-isolated vapors of XVO<sub>3</sub> (X = Na, K, Rb, and Cs)<sup>3</sup> whose results have been interpreted in terms of the two main components of the vapors, XVO<sub>3</sub> and XVO<sub>2</sub> monomeric species both having a  $C_{2v}$  ring structure.

A better possible interpretation of these results has been provided by a more recent multitechnique (thermogravimetry, mass spectroscopy, IR matrix isolation, and standard solid analysis techniques) study of the  $CsVO_3$  vaporization.<sup>4</sup> In this work, however, a coherent explanation of all the experimental information available at the time was reached only by resorting to many assumptions which, in some cases, needed further inquiries.

The mass spectrometric results for  $KVO_3^5$  and those for the remaining alkali-metal metavanadates, which are very preliminary and not yet published, outline a very similar situation as for CsVO<sub>3</sub>, and therefore the present work has been undertaken with the following main purposes: (i) try to clarify the points still questionable in the CsVO<sub>3</sub> data interpretation; (ii) check the extensibility of the conclusion drawn for CsVO<sub>3</sub> to the entire class of compounds; and (iii) get as much structural information as possible about the species identified.

## **Experimental Section**

1. Metavanadates Sample Preparation. Powders of  $V_2O_5$  (99% pure from Koch & Light),  $Li_2CO_3$ ,  $K_2CO_3$ , and  $Cs_2CO_3$  (ultrapure reagent grade from Ventron),  $Na_2CO_3$  (99.5% pure from Carlo Erba), and  $Rb_2CO_3$  (99.9% pure from Strem Chemicals Inc.) were the starting materials for sample preparation.

After separate preheating of several hours at 300 °C in a muffle furnace, stoichiometric amounts of  $V_2O_5$  and of the proper carbonate were mixed in a porcelain container, brought, in the same furnace, to a temperature T a little beyond the corresponding

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#### Alkali-Metal Metavanadate Monomers and Dimers

metavanadate melting point, and kept at this temperature for 1 h.

After cooling at room temperature, the solidified melts were accurately ground to powder. The procedure of heating up to Tpowders and grinding solidified melts was repeated in order to obtain a more homogeneous composition of the samples. The formation of the required metavanadate phases was ascertained through X-ray analysis and, whenever possible, SEM techniques. A further confirmation of the suitability of the samples prepared for the present work comes from the reproducibility of the X-ray and IR spectra when commercial samples of NaVO<sub>3</sub> (>98% pure from Fluka) were used.

2. Experimental Apparatus and Technique. The experimental apparatus is basically constituted of a Bruker IFS 113v interferometer coupled with a Displex 202 CSA (Air Products and Chemicals) rotatable under vacuum ( $10^{-6}$  Torr) in a stainless steel homemade shroud. This is, in turn, coupled, under high vacuum, with a homemade high-temperature furnace. Details on the apparatus components and technqieus employed for heating Knudsen cells, reading temperatures, trapping vapors in cold matrices of constant (10 K) temperature, and getting their IR reflectance spectra have been reported elsewhere.<sup>4</sup> Here again Pt-Rh 13% was preferentially used as the crucible material.

Attempts at using Mo or Ta and reproducing the reported<sup>3</sup> changes in the IR spectra in going toward greater reduction of vaporization conditions failed since no spectrum could be obtained. Pt powder was also added to the samples in order to prevent the effect of creeping phenomena out of the Knudsen cells, which is particularly important in the case of Li and Na compounds.

Two different types of experiments were performed according to whether single metavanadate powders or their mixtures were used as vaporizing samples. All pure metavanadate samples were vaporized at least at three different temperatures in a range suitable for measurement of spectral band growth rates temperature dependence (SBGRTD). In experiments on mixtures, which concerned the couples  $XVO_3$ -CsVO<sub>3</sub>, with X = Li, Na, K, and Rb, a common vaporization temperature around 1450 K was selected in the effort of obtaining, as long as possible, spectral bands with enough intensity for the less volatile component without saturation for the more volatile one. In order to obtain infrared spectra of comparable intensities the deposition time was varied according to the sample nature and the vaporization temperature, the values adopted ranging from 1 to 4 h.

In taking into account the different quality of the CsVO<sub>3</sub> spectra we obtained when different isolating gases were used,<sup>4</sup> nitrogen was employed in all the present experiments, although argon was occasionally used for the sake of control. In any case, the high pure gas flow, controlled by a standardized needle valve, was maintained at a constant value of 1 mmol/h for optimal isolating conditions.

In all cases 200 scans spectra were accumulated in the middle  $(4000-400 \text{ cm}^{-1})$  and far infrared region  $(400-150 \text{ cm}^{-1})$  with a resolution never lower than 1 cm<sup>-1</sup>.

#### **Results and Discussion**

Due to the number of different topics in this section, the results of pure compound vaporization studies, those of mixture vaporization studies, and the argument concerning the symmetries of the identified species will be treated separately.

1. Pure Compound Vaporization Results. The temperature ranges explored were, in K, 1680–1840 for LiVO<sub>3</sub>, 1490–1810 for NaVO<sub>3</sub> and KVO<sub>3</sub>, 1440–1840 for RbVO<sub>3</sub>, and 1310–1470 for CsVO<sub>3</sub>.

The general features of the spectral patterns and of their changes with the temperature were quite similar for all the metavanadates. Therefore, only the  $KVO_3$  spectra recorded at two different temperatures (1520 and 1810 K) have been reported in Figure 1, as representative of the whole class.

The frequencies of the observed absorption bands of XVO<sub>3</sub> (X = Li, Na, K, and Rb) isolated in N<sub>2</sub> matrices are reported in Table I, together with the proposed assignment. For the sake of comparison, the corresponding data obtained in our previous work for



Figure 1. Vanadium-oxygen stretching modes of nitrogen-isolated  $KVO_3$  vaporized at 1520 K (---) and 1810 K (--).

TABLE I: Frequency Values (cm<sup>-1</sup>) of Vanadium-Oxygen Stretching Modes of Nitrogen Matrix-Isolated Alkali-Metal Metavanadates

LiVO <sub>3</sub>	NaVO <sub>3</sub>	KVO <sub>3</sub>	RbVO <sub>3</sub>	CsVO <sub>3</sub>	assignment
				961.9 sh	
954.7 ms	948 m	960.7 s	960.2 s	958.1 s	V=O (d)
951.8 sh	944.1 s	957.1 sh	958.8 sh		
934.9 m	937.8 m	937.2 m	934.9 m	939.8 m	V=0 (m)
		933.5 sh	934.7 sh		
896. sh					
890.8 ms	903.1 m	906.2 s	906.7 s	905.5 s	V=O (d)
	900.9 m	903.6 sh	905.3 sh	904.3 sh	
883.6 mw	894.2 ms	900. mw	897.6 m	896.1 mw	V=O (m)
	890.6 m				
	876.6 m				? (see text)
		710. vw	710.9 w	709.3 w	V-O (d)
678.9 w	677.2 w	689.7 ms	688.8 m	684.9 m	V–O (d)
		667.1 m	666.6 mw	663.7 mw	V-O (d)

a m = monomer; d = dimer.

 $CsVO_3^4$  are also reported in the same table. As shown in the table, the only appreciable deviation from the above-cited similarity consists in the number of bands observed in the spectral region 870–970 cm<sup>-1</sup> which for NaVO<sub>3</sub> resulted to be three instead of two.

In spite of the many possible implications of this finding, the extreme one of an NaVO<sub>3</sub> overall process quite different from that of the remaining metavanadates, and therefore requiring a completely different interpretation of the spectra, is at present discarded on the basis of the preliminary mass spectrometric data and of all the analogies in the NaVO<sub>3</sub> and other metavanadates' spectral patterns which concern features other than those brought into question.

The analogies in the results obtained for different metavanadates and their possible implications can be summarized in the following points:

1. Regardless of the nature of the evaporated sample, how high the temperature was, and how long the time of deposition was (up to 4 h in some cases, as already reported), the matrices' transparency was always maintained. This finding allows one to extend to all the metavanadates the conclusion already drawn for  $CsVO_3^4$  that contributions to the metavanadates' overall vaporization process from possible mechanisms of dissociative vaporization leading to the formation of gaseous monoatomic alkalimetal species, if present, are of minor importance.

Further support for this conclusion comes from the fact that bands over 1000 cm<sup>-1</sup> corresponding to possible decomposition partners like VO and VO<sub>2</sub> molecules could be observed only in spectra taken at vaporization temperatures near the upper limit of the range explored and always with very weak intensities.

2. In all the recorded spectra, even in the case of saturated bands, no modes more strongly dependent on the alkali metal than those reported in Table I could be observed. This and the fact that all the observed bands other than the VO and VO<sub>2</sub> bands lie in two restricted regions at frequencies 870-970 and 650-700 cm<sup>-1</sup> (according to literature data<sup>1-3</sup> characteristics of V=O and V-O bonds stretching, respectively) led us to conclude that, for all the metavanadates, the observable spectral pattern arises from bond stretching motions of V and O containing groups scarcely influenced by the alkali-metal presence.

3. For all the metavanadates the spectra at the lower end of the proper vaporization temperature ranges are quite simple and mainly consist of four bands of strong and medium intensities at 960.7, 906.2, 689.1, and 667.1 cm<sup>-1</sup>, which are the same bands observed in previous IR and/or Raman studies on metavanadates.<sup>3,4</sup> The arguments on the growth rate's temperature dependence and its possible correspondence to the parent ion's temperature dependence in the mass spectra, used for assigning the corresponding bands in our previous work on CsVO<sub>3</sub> still held for KVO<sub>3</sub>, can be reasonably assumed for the remaining metavanadates. Here again, the limits of these arguments have been proved since they failed to assign to the dimer the bands at 689.7 and 667.1 cm<sup>-1</sup>, as correctly made by comparison of spectra obtained in pure and mixed compound vaporizations (see below).

Of the minor bands observed in the high-intensity/low-temperature range, those at 937.2 and 890.9 cm<sup>-1</sup> could be definitely assigned (see below) to the monomer while in the absence of further proofs for or against, the band at 710.0 cm<sup>-1</sup> was tentatively attributed to the dimer as already made in the CsVO<sub>3</sub> case.<sup>4</sup>

4. In all cases, the spectral complexity was found to increase with the vaporization temperature mainly due to the presence of strong bands at 937.2 and 900.0 cm<sup>-1</sup>, with growth rates increasing much faster with the temperature than the "lower temperature bands". Here again the strict similarity of their temperature dependence led us to assign them to a unique species. Moreover, since for KVO<sub>3</sub>, as already found for CsVO<sub>3</sub>, the common temperature dependences of the above bands match well that of the corresponding monomer parent ion in their mass spectra,<sup>4,5</sup> and in view of the analogies in the different metavanadates spectra, the unknown species is very likely always identifiable with the monomer. Such an assumption for KVO<sub>3</sub>, RbVO<sub>3</sub>, and CsVO<sub>3</sub> could be definitely proved by the mixed compound vaporization results in the following section.

2. Mixed Compound Vaporization Results. Such types of experiments have been performed as an alternative to isotopic substitution, at least at the end to ascertain the number of atoms in the main components of the metavandate vapors. Indeed, the attempts we made to obtain <sup>18</sup>O-enriched alkali-metal metavandates (either directly for isotopic exchange reaction of the metavanadates samples in solution of  $H_2$ <sup>18</sup>O or in trying to obtain <sup>18</sup>O-enriched V<sub>2</sub>O<sub>5</sub> and use it in the metavanadates sample preparation) gave a yield too low for producing appreciable bands in a spectral region in which bands tend to be crowded and overlapped.

Instead, bands arising from the substitution of a different X' alkali metal element in the frame of a polymeric XVO<sub>3</sub> species could be easily observed when the couples  $KVO_3$ -CsVO<sub>3</sub> and RbVO<sub>3</sub>-CsVO<sub>3</sub> were simultaneously vaporized at 1450 K. The spectral patterns obtained in the two cases (the only ones performed successfully until now) were quite similar to that reported in parts a and b of Figure 2 for the couple  $KVO_3$ -CsVO<sub>3</sub>. Four substitution bands have been observed, at frequencies of (cm<sup>-1</sup>) 959.8, 905.8, 686.9, and 666.1 for the couple  $KVO_3$ -CsVO<sub>3</sub> and 959.0, 905.9, 686.1, and 665.2 for the couple RbVO<sub>3</sub>-CsVO<sub>3</sub>.



Figure 2. Infrared spectra of codeposited potassium and cesium metavanadates: (a, top) V=O stretching modes of  $(KVO_3)_2 (\dots)$ ,  $(CsVO_3)_2$ (---), and  $KCs(VO_3)_2 (\dots)$ . (b, bottom) V-O stretching modes of  $(KVO_3)_2 (\dots)$ ,  $(CsVO_3)_2 (---)$ , and  $KCs(VO_3)_2 (--)$ .

Unaffected intense modes have also been detected which proves the presence in the vapors of two different main components, one of them involving no more than one alkali-metal atom. Since these modes correspond to those attributable to the monomer according to SBGRTD arguments, the existence of the monomer as species tending to prevail at high temperatures appears to be definitely proved.

On the other hand, the fact that no more than one substitution band for each mode could be detected definitely assigns to the dimer the bands at 960.7, 906.2, 689.7, and 667.1 cm<sup>-1</sup> and excludes the presence in the vapors of appreciable amounts of higher polymers.

No substitution bands could be detected for the modes lying at 710.0  $\text{cm}^{-1}$  which was previously assigned to CsVO<sub>3</sub> dimer.<sup>4</sup> Since this failure is well explainable because of its low intensity,

In any case the presence of only monomers and dimers as main components of the vapors is proved as well as the fact that at low temperatures the metavanadates preferentially vaporize as dimeric species.

3. Symmetry Considerations. 3.1. Monomeric Species. No argument in favor of one or the other of the two structures hypothesized in the past for the CsVO<sub>3</sub> monomer, both of planar  $C_{2v}$  symmetry but with different (mono- or bidentate) coordination of the VO<sub>3</sub><sup>-</sup> anion, could be obtained by the present results. Since these results led us to reject the arguments in ref 3 as based on an incorrect assignment to the monomer of bands to be attributed to the dimer, no experimental information is at the moment, available on the monomer's structure.

The only theoretical information comes from ab initio calculations very recently performed on the  $LiVO_3$  monomer which indicate as more energetically stable the bidentate structure.<sup>6</sup>

Therefore, there is a strong suggestion for extending this conclusion to the whole class of alkali-metal metavanadate gaseous monomeric species. Some support comes also from the existence of monomers with a bidentate structure for analogous classes of alkali-metal compounds (e.g., nitrates, phosphates, and carbonates), experimentally ascertained through comparison of Raman and IR spectra or <sup>18</sup>O isotopic shift measurements.

In this assumption, however, unusually high rearrangement energies must be invoked to explain the rather high mass spectrometric values reported for the  $KVO_3^5$  and  $CsVO_3^4$  dimerization energies.

In fact, the literature data on X–O bond energy values in different X gaseous oxides like XO, XO<sub>2</sub>, and  $X_2O_2$  (X = K, Cs) show that the dimerization energies are comparable with and possibly higher than the energy required for the formation of two X–O bonds while the formation of a dimer starting from bidentate monomers requires only a rearrangement of already existing bonds.

3.2. Dimeric Species. With the band assignments made possible by the present results, the spectra in ref 3 can be entirely interpreted in terms of a dimeric species.<sup>4</sup>

These findings, if not introducing new arguments, provide a much more better grounds to those used in ref 4 for ruling out possible  $D_{2h}$  symmetries.

The presence in both Raman and IR spectra of five bands at very close frequencies of 960.7, 710.0, and 670 cm<sup>-1</sup> (totally symmetric) and at 906.2 and 689.7 cm<sup>-1</sup> (depolarized) cannot be suspected to be a fortuitous coincidence. Therefore, there is now much more evidence for ruling out  $D_{2h}$  symmetry than previously.<sup>4</sup> With respect to the discussion made therein, we can add that a lowering of the symmetry to  $C_2$ , for which differently polarized V=O modes are not expected, must be ruled out. This definitely leads to the  $C_{2v}$  symmetry as the one most compatible with the available spectroscopic data.

(6) Bencivenni, L.; Ramondo, F. Private communication.

The new results cannot provide further information on which of the many conceivable structures of the  $C_{2v}$  symmetry is to be preferred. Therefore, now, as before, the only available arguments are of the following types:

1. Chemical reasons, which seem to favor three types of structures, i.e., the one proposed previously<sup>4</sup> and those obtainable by distortion of two three-ring-containing structures, one of which is planar and one with the vanadium in a tetrahedrically coordinated position.

2. The results of the ab initio calculations on  $LiVO_3$  already cited, which, by analogy, led us to prefer structures which maintain the  $VO_3^-$  planarity.

3. The features of the fragmentation pattern on electronic bombardment resulting from the mass spectra of  $KVO_3^5$  and  $CsVO_3^4$  either as it concerns the nature of the fragment ions observed or the energetics of their formation (as it results from the measured appearance potentials of the ions in question) which favors structures like that already hypothesized for  $CsVO_3$ .<sup>4</sup> With these types of structures, indeed, the mass spectrometric data can be simply explained in terms of bond breaking.

### Conclusions

The new results allow a coherent satisfactory interpretation not only of all the Raman and IR data until now available for gaseous alkali-metal metavanadates but also of the information from other techniques.

Particularly satisfactory is the possibility of explaining "the low-temperature spectra" of  $CsVO_3$  without hypothesizing as previously made<sup>3,4</sup> the presence of a  $CsVO_2$  species as a main component of the vapors.

The explanation of this presence, indeed, was not easily justifiable under the vaporization conditions of ref 4, and in effect the explanation given was only attempted on the basis of the rather questionable assumption that the creeping of the liquid caused part of the sample to evaporate out of the crucible and possibly into contact with the tantalum resistors.

According to the present interpretation, the existence of stable gaseous  $XVO_3$  monomer and dimer species is definitely proved for X = K, Rb, and Cs, and reasonably inferred for X = Li and even, with some more uncertainty, for X = Na.

With the same degree of confidence in the various cases, the presence of both monomers and dimers as the main components of the vapors confirms the substantial congruence of the  $KVO_3^5$  and  $CsVO_3^4$  vaporization process and allows us to extend such a conclusion to the entire class of metavanadates.

Moreover, a  $C_{2\nu}$  symmetry has been proposed for the dimers and for the first time, mixed gaseous dimers with different alkali-metal atoms in their frame, like KCs(VO<sub>3</sub>)<sub>2</sub> and RbCs(VO<sub>3</sub>)<sub>2</sub>, could be also identified.

**Registry No.**  $LiVO_3$ , 15060-59-0; NaVO\_3, 13718-26-8; KVO\_3, 13769-43-2; RbVO\_3, 13597-45-0; CsVO\_3, 14644-55-4;  $Li_2(VO_3)_2$ , 131906-46-2; Na<sub>2</sub>(VO<sub>3</sub>)<sub>2</sub>, 131906-47-3; K<sub>2</sub>(VO<sub>3</sub>)<sub>2</sub>, 131906-48-4; Rb<sub>2</sub>(V-O<sub>3</sub>)<sub>2</sub>, 131906-49-5; V<sub>2</sub>O<sub>5</sub>, 1314-62-1;  $Li_2CO_3$ , 554-13-2; K<sub>2</sub>CO<sub>3</sub>, 584-08-7; Cs<sub>2</sub>CO<sub>3</sub>, 534-17-8; Na<sub>2</sub>CO<sub>3</sub>, 497-19-8; Rb<sub>2</sub>CO<sub>3</sub>, 584-09-8; KCs-(VO<sub>3</sub>)<sub>2</sub>, 131906-50-8; RbCs(VO<sub>3</sub>)<sub>2</sub>, 131906-51-9; N<sub>2</sub>, 7727-37-9.