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The gas-phase on-line production of vanadium oxytrihalides, VOX_3 and their identification by infrared spectroscopy

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Abstract

A new route has been devised, leading to the production of VOX_3 molecules where X=F, Br and I by an on-line process using vanadium oxytrichloride, $VOCl_3$ as a starting compound passed over the following heated salts NaF, KBr and KI at 375, 700 and 550°C, respectively. The products have been characterized by the IR spectra of their vapors. The low resolution gas phase on-line Fourier transform infrared spectra reported for the first time show strong bands with PQR type structure, centered at 1058, 1035, 1030 and 1025 cm^{-1} assigned to the $\nu_1(a_1)$, the O=V stretching fundamental mode of VOF_3, $VOCl_3$, $VOBr_3$ and VOI_3, respectively. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The oxohalides of vanadium compounds are generally prepared from the oxides but are not particularly well known. They are limited almost entirely to the oxidation states of + 4 and + 5. The oxidation state + 5, such as VOX_3 and VO_2X where X is a halogen, is relatively stable. The + 4 oxidation state vanadium oxohalides compounds such as VOX_2 are notably hydroscopic and hydrolyze vigorously to the hydrous pentoxide. The chemical and physical properties of VOX_3, VO_2X and VOX_2 have been reported by Greenwood and Earnshaw [1].

The vanadium oxytrihalides, VOX_3 are expected to have C_{3v} symmetry by comparison with the phosphoryl halides, POX_3 [2]. Therefore, there must be six fundamentals modes, all infrared and Raman active. Three of these are totally symmetric vibrations, of species a_1, and three are doubly degenerate vibrations of species e. In the infrared spectrum, the former show up as parallel type bands and the latter as perpendicular bands.

Selig and Claassen recorded the infrared spectrum of VOF_3 vapour and interpreted the molecule in terms of C_{3v} symmetry and all six fundamentals were observed [3]. The infrared spectra of the liquid and the gaseous Raman spectra of $VOCl_3$ have been reported by Miller and Ozin [4,5].

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The infrared spectrum of liquid $VOBr_3$ has been recorded from 75 to 3000 cm^{-1} [6].

The gas phase on-line production of the analogous species, POX_3 where X=F, Cl, Br and I and their identification by infrared spectroscopy have been reported [2]. Continuing our previous observations and the recent work regarding the antimony oxide trihalides, $SbOX_3$ [7], this paper investigates the on-line production of vanadium oxytrihalides, VOX_3 where X=F, Br and I and their gas phase IR spectra, which have not been reported previously, using $VOCl_3$ as a starting material passed over heated NaF, KBr and KI for VOF_3, $VOBr_3$ and VOI_3 production, respectively. It should be mentioned that no previous experimental and spectroscopic data for VOI_3 are available and the reported results can be considered as the first attempt to investigate such a molecule.

2. Experimental

The first step was to optimize the production conditions of vanadium oxytrichloride, $VOCl_3$, in order to carry on observing the VOF_3, $VOBr_3$ and VOI_3 infrared spectra by on-line process using $VOCl_3$ as starting material. $VOCl_3$ (Fluka, 99.9%) was first degassed in the vacuum line using liquid nitrogen. The on-line process involved heating the $VOCl_3$ with heating tape to about 40°C to obtain enough vapor pressure and the vapor was passed via a vacuum line into an IR cell fitted with two KBr windows. The remaining conditions were fast flow, 2 cm^{-1} resolution and under 0.5 torr pressure. The yellow color of $VOCl_3$ material was seen in the IR cell.

The synthesis routes for VOF_3, $VOBr_3$ and VOI_3 can be written as follows:

$$VOCl_{3(g)} + 3NaF_{(s)} \xrightarrow{375°C} 3NaCl_{(g)} + VOF_{3(g)}$$

$$VOCl_{3(g)} + 3KBr_{(s)} \xrightarrow{700°C} 3KCl_{(g)} + VOBr_{3(g)}$$

$$VOCl_{3(g)} + 3KI_{(s)} \xrightarrow{550°C} 3KCl_{(g)} + VOI_{3(g)}$$

The salts containing halogens used in these experiments were obtained from Aldrich with a purity of 99.9%. The final reaction colors from the above three syntheses were yellow, deep red and pink, respectively.

The products from these reactions were passed directly into an IR cell (15 cm path length) fitted with two KBr windows. A similar experimental set-up was used in the previous work [2]. The distance between the heated furnace and the IR cell was about 3 cm. The cell was pumped out via a liquid nitrogen trap with a rotary pump (RV8, Edwards) displacing 8.5 m^3 h^{-1}. The IR spectra were recorded on a JASCO 300E FTIR spectrometer at a resolution of 2 cm^{-1}. Regarding the VOI_3, the experiment was performed at 1 cm^{-1} in order to resolve its O=V stretching band.

3. Results and discussion

Fig. 1 shows the infrared spectra of $VOCl_3$ (top) and $POCl_3$ (bottom). The top spectrum is the result of heating the $VOCl_3$ only with heating tape to

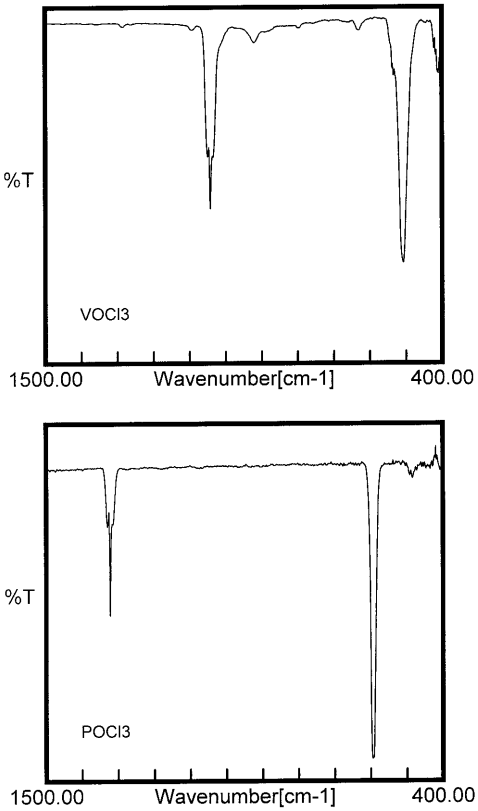

Fig. 1. The gas phase infrared spectra of $VOCl_3$ (top) and $POCl_3$ (bottom) in the range (400–1500) cm^{-1}.

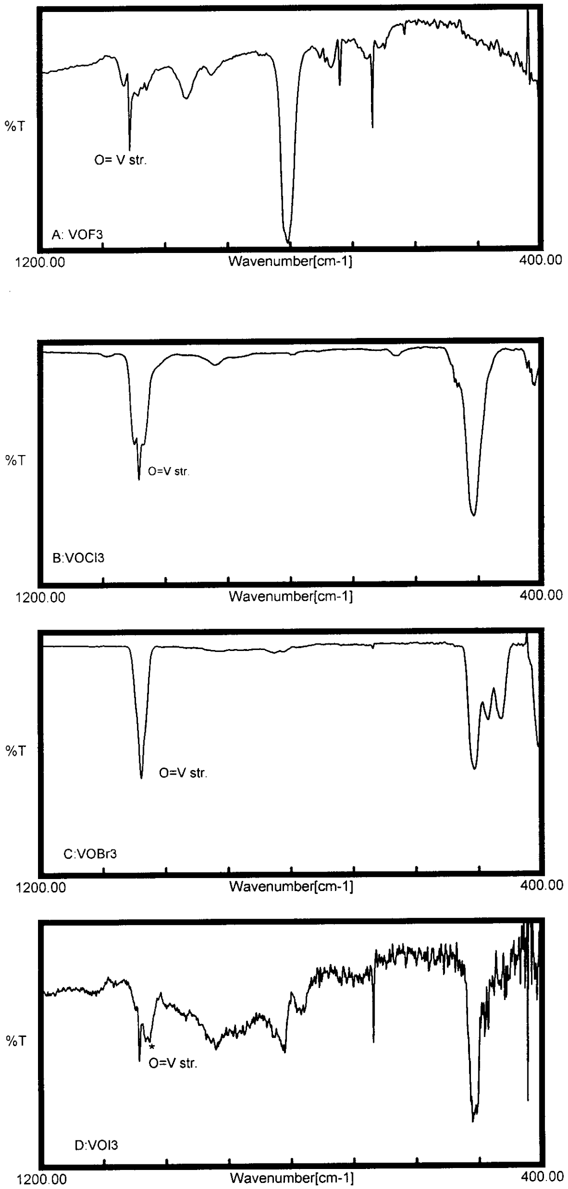

Fig. 2. Full gas phase infrared spectra of VOX_3 where X=F, Cl, Br and I in the range (400–1200) cm^{-1}.

about 40°C to obtain enough vapor pressure. Three strong bands were observed in the spectrometer range (400–4000 cm^{-1}) at 1035, 505 and 408 cm^{-1}. The first band centered at 1035 cm^{-1}, is assigned to the $\nu_1(a_1)$, the O=V stretching mode of $VOCl_3$ and shows typical PQR-type structure and with a strong Q-head. The second band at 505 cm^{-1} is assigned to the $\nu_4(e)$, mode of $VOCl_3$. The last band centered at 408 cm^{-1} is assigned to the $\nu_2(a_1)$, the VCl_3 umbrella mode of $VOCl_3$. These results are identical to those observed by gas phase Raman spectroscopy at 1035, 504 and 408 cm^{-1}, respectively [5]. The bottom spectrum is presented here for comparison only. An identical type of structure was observed for the O=P stretching mode of $POCl_3$ [2] $\nu_1(a_1)$. The band is centered at 1312.9 cm^{-1} where the second band at 590 cm^{-1} is assigned to the $\nu_4(e)$, fundamental of $POCl_3$.

Fig. 2 shows three new spectra A, C and D (400–1200 cm^{-1}) where spectrum B is the precursor ($VOCl_3$). Spectrum A is the result of passing $VOCl_3$ gas over heated NaF at 375°C. The three characteristic bands of VOF_3 were observed within the spectrometer range used at 1058, 806 and 722 cm^{-1}. This spectrum fits very well with that expected. The two bands centered at 1058 and 722 cm^{-1} each have the sharp Q branch characteristic of parallel bands. Similarly, the band at 806 cm^{-1} can clearly be assigned as a perpendicular, or species (e), band because it does not have a strong Q branch. Therefore, the first band at 1058 cm^{-1} can be assigned to $\nu_1(a_1)$, the O=V stretching mode of VOF_3.

This result is consistent with expectations and the band is shifted to higher frequency when fluorine replaces the chlorine in $VOCl_3$ to form VOF_3 which is similar to the POX_3 study [2]. The second band at 806 cm^{-1} is assigned to the $\nu_4(e)$, the V–F stretching mode of VOF_3. The third band at 722 cm^{-1} is assigned to the $\nu_2(a_1)$, the VF_3 umbrella mode of VOF_3 and this band has a PQR-type structure as expected. The last band shown in the spectrum at 673 cm^{-1} is assigned as a combination band $2\nu_6(e)+\nu_3(a_1)$ of VOF_3. Our infrared spectrum results for VOF_3 are in excellent agreement with the previous gas phase infrared results [3] after VOF_3 was prepared by the method of Trevorrow using V_2O_5/HF [8]. Their observed frequencies were at 1057.8, 806 and 721.5 cm^{-1}, respectively [3]. Note that the observed frequencies are identical to those observed before using two different methods of preparation.

Having confirmed the existence of VOF_3 by the new route, the next step was to generate and observe the infrared spectrum of $VOBr_3$. Spectrum C in Fig. 2 is the result of passing $VOCl_3$ gas over heated KBr at 700°C. Two new bands were observed within the spectrometer range used at 1030, and 400 cm^{-1}. The first band at 1030 cm^{-1} is assigned to $\nu_1(a_1)$, the O=V stretching mode of $VOBr_3$. This result is consistent with expectation and the band is shifted to lower frequency when the bromine replaces the chlorine in $VOCl_3$ to form $VOBr_3$. Once again, the band shows typical PQR-type structure with a strong Q-head. The second band at 400 cm^{-1} is assigned to the $\nu_4(e)$ mode of $VOBr_3$. The third band in the spectrum is due to the precursor, $VOCl_3$. Miller and Baer have recorded the infrared spectrum of liquid $VOBr_3$ [6]. Therefore, the obtained gas phase IR results for $VOBr_3$ can be compared with the infrared spectrum of liquid $VOBr_3$ after the following synthesis:

$$V_2O_5 + 2H_2 \xrightarrow{500°C} V_2O_3 + 2H_2O$$

$$V_2O_3 + 3Br_2 + C \xrightarrow{200°C} 2VOBr_3 + CO$$

The O=V stretching mode of $VOBr_3$, which was generated by our on-line method in comparison with those of liquid production is shifted 5 cm^{-1}. This may be due to the fact that the two spectra were generated from different phases.

The final step is shown in Fig. 2 (spectrum D) which is the result of passing $VOCl_3$ gas over heated KI at 550°C. The gas phase infrared spectrum of VOI_3 is recorded here for the first time and no other spectroscopic data are available. Because there are no previous experimental spectroscopic data for VOI_3, the assignment of the new spectrum can be analyzed considering the previous analogous molecules. It should be mentioned here that the production of pure VOI_3 is also difficult due to easy sublimation of iodine at the high temperature of heated KI. Nevertheless, the most characteristic band of VOI_3 is observed. This band is positioned to the right side of the $VOCl_3$ band and centered at 1025 cm^{-1} and assigned to the $\nu_1(a_1)$, the O=V stretching mode of VOI_3. The observed band has a PR-type structure and this experiment has been performed under 1 cm^{-1} as the lowest available resolution in our spectrometer in order to resolve this structure. The PR profile can be seen in spectrum D (Fig. 2), the Q-head was not observed and a high resolution spectrum would reveal the structure of the band. It seems to be that in some stages of the reaction $VOCl_2I$ or $VOClI_2$ may be formed before VOI_3 formation and this could explain the other bands shown in spectrum D. Therefore, it can be said that the other peaks shown in the VOI_3 spectrum are due to the impurities, which were

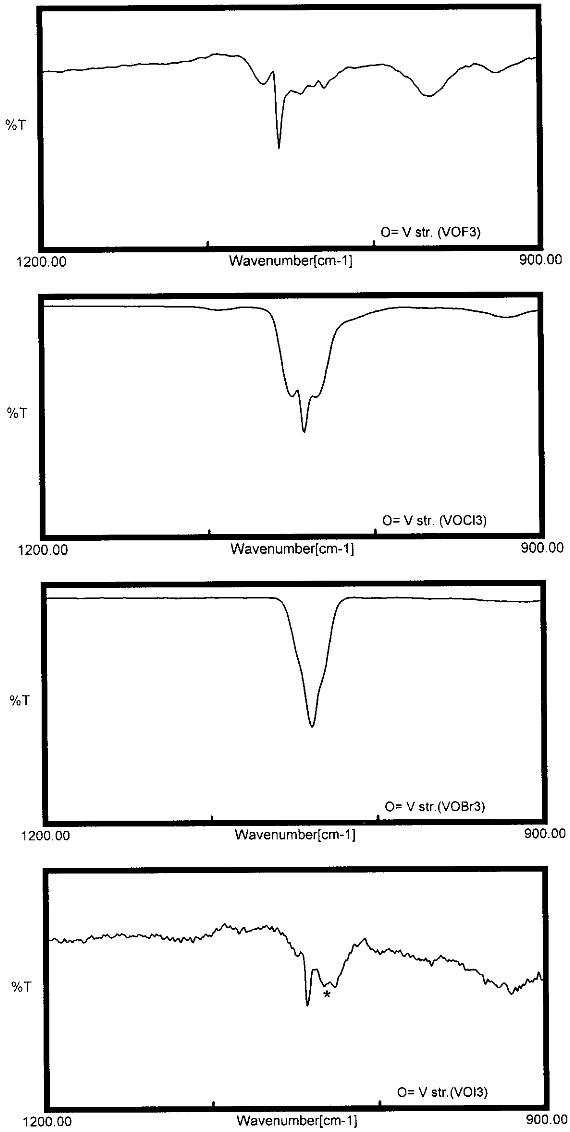

Fig. 3. The $\nu_1(a_1)$, the O=V stretching mode of VOX_3 where X=F, Cl, Br and I in the range (900–1200) cm^{-1}.

Table 1
Observed gas phase IR frequencies of VOX_3, in comparison with other results including the P–R separation (cm^{-1})

Molecule	Mode	Assignment	Observed		P–R separation	
			Related results	This work (IR) gas-phase on-line production	Obs.	Calc.
VOF_3	ν_1	a_1(O=V str.)	1057.8[a]	1058	19.0	18.3
	ν_4	e(V–F str.)	806	806		
	ν_2	a_1 VF_3 umbrella	721.5	722		
	ν_3	a_1 FVO def.	257.8	–		
	ν_5	e(O=VF_3 rock)	308	–		
	ν_6	e(VF_3 def.)	204.3	–		
$VOCl_3$	ν_1	a_1(O=V str.)	1035[b]	1035	16.0	15.7
	ν_4	e(V–Cl str.)	504	505		
	ν_2	a_1 VCl_3 umbrella	408	408		
	ν_3	a_1 ClVO def.	165	–		
	ν_5	e(O=VCl_3 rock)	249	–		
	ν_6	e(VCl_3 def.)	129	–		
$VOBr_3$	ν_1	a_1(O=V str.)	1025[c]	1030	12.1	12.0
	ν_4	e(V–Br str.)	400	400		
	ν_2	a_1 VBr_3 umbrella	271	–		
	ν_3	a_1 BrVO def.	120	–		
	ν_5	e(O=VBr_3 rock)	212	–		
	ν_6	e(VBr_3 def.)	83	–		
VOI_3	ν_1	a_1(O=V str.)	–	1025	6.0	5.3
	ν_4	e(V–I str.)	–	–		
	ν_2	a_1 VI_3 umbrella	–	–		
	ν_3	a_1 IVO def.	–	–		
	ν_5	e(O=VI_3 rock)	–	–		
	ν_6	e(VI_3 def.)	–	–		

[a] Gas phase infrared spectrum of VOF_3 applying another route of production.

[b] Raman spectrum of gaseous $VOCl_3$.

[c] Infrared spectrum of liquid $VOBr_3$ applying another method of production.

originated from $VOCl_3$. Fig. 3 shows $\nu_1(a_1)$, the O=V stretching mode of VOX_3 where X=F, Cl, Br and I in the range (900–1200) cm^{-1}. It should be pointed out here that the left-hand side of $\nu_1(a_1)$ in VOI_3 spectrum (Fig. 3) is due to the $\nu_1(a_1)$ of $VOCl_3$.

All the observed frequencies (cm^{-1}) of VOF_3 determined by this gas phase infrared spectroscopy work in comparison with the data obtained by gas and liquid phase of VOF_3 and $VOBr_3$, respectively are listed in Table 1 including the observed and calculated values of PR separation using the method of Paul and Dijkstra [9] for the $\nu_1(a_1)$ VOX_3 where X=F, Cl, Br and I. It is concluded that the present work reports for the first time, the gas phase on-line production and detection of VOX_3 using the FTIR technique. Our experimental data agree with the expectation and a satisfactory trend was observed. Our results are compared with previous study regarding the gas phase infrared spectrum of VOF_3 and $VOCl_3$ and also with the infrared spectrum of liquid $VOBr_3$. The observed results are in excellent agreement with previous reported work.

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