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RAMAN STUDY OF THE O_2F_2 + VF_5 REACTION: ISOLATION AND IDENTIFICATION OF AN UNSTABLE REACTION INTERMEDIATE

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SUMMARY

The reaction of O_2F_2 with polymeric VF_5 in the temperature range -119 to -78°C leads first to the reaction intermediates $F{-}O\cdots O^{\delta+}\underline{\cdots}F^{\delta-}\cdots V_2F_{10}$ or $O_2F^+ + F^- + V_2F_{10}$. On increasing the temperature of this intermediate, a new compound $O_2^+V_2F_{11}^-$ is formed which in turn decomposes rapidly at room temperature. Raman studies of these species as well as of O_2F_2(solid), VF_5, KVF_6, KV_2F_{11}, $CsVF_6$ and CsV_2F_{11} are reported and discussed.

INTRODUCTION

Compounds containing the dioxygenyl cation O_2^+ have been synthesized thermally, [1-7] photolytically [8-12] and by discharge techniques. [3,13-17] The earliest involved the room temperature oxidation of molecular oxygen with platinum hexafluoride [1,2] to form O_2PtF_6. Syntheses directly from the elements, [4-7] using mixtures of fluorine and oxygen and a fluorine containing species MF_n [1-3,8-12] or using reactive

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species such as O_2F_2, O_4F_2, OF_2 and $(O_2F)_n$ [13-17] have all proved to be useful. The products are normally formulated as $O_2MF_n (n=4,5,6)$, $O_2M_2F_{11}$ or $O_2M_3F_{16}$. Examples include O_2BF_4, [14,15,17] O_2GeF_5, [11] O_2AsF_6, [3,4,8,9,13,18] O_2PtF_6, [1,2,4,18,19] O_2AuF_6, [6,7,18] $O_2Sb_2F_{11}$, [4,10,12,18] and $O_2Sb_3F_{16}$. [20] All of these dioxygenyl salts are intrinsically unstable thermally with room temperature lifetimes varying from a few minutes to several weeks. [13-17,21] Examples of possible expected dioxygenyl salts that have not been made include O_2IrF_6 and O_2OsF_6.[22] Compounds such as O_2PF_6 [13] O_2CrF_6 and $O_2V_2F_{11}$ [23] are very unstable at room temperature and may need to be studied at reduced temperature. They have been identified through analysis of their decomposition products or through spectroscopic observations.

Dioxygenyl salts containing vanadium were particularly intriguing. Using a conventional synthesis from the elements, [4] a thermally unstable oxygen containing product of unknown composition could be prepared, isolated and manipulated in a dry box. Unfortunately the sample suffered rapid decomposition near 20°C. The manipulation time required was always a little too long and the decomposition a little too rapid to allow us to do definitive experiments with the white solid product. The O_2^+ ion was readily identified from its characteristic Raman spectrum but a positive identification of the corresponding anion remained elusive. Syntheses at lower temperatures were impractical because the reaction rate was too slow. Therefore, the reaction of the thermally unstable O_2F_2 species with the strong fluoride acceptor molecule VF_5 at low temperatures seemed to offer an attractive route to O_2VF_6 or $O_2V_2F_{11}$, neither of which had been characterized in the chemical literature.

During the course of this work, the details of which are given in the following sections, $O_2V_2F_{11}$ was prepared and characterized by its Raman spectrum. In addition, a highly reactive and unstable intermediate cation has been identified and formulated as $F{-}O\overset{\cdots}{-}O^{\delta+}$ where δ approaches unity and may in fact be one. The corresponding anion is not $V_2F_{11}^-$. It has been formulated tentatively as $\overset{\delta-}{F}\cdots V_2F_{10}$ where δ also approaches or is equal to unity.

Starting materials, reactive intermediates, products and related compounds were all examined in detail using Raman spectroscopy, often as a function of temperature. Solid O_2F_2 was reexamined because of uncertainties and ambiguities in earlier work.[24-28] The present study confirms the results and interpretation of Gardiner et al.[24]

EXPERIMENTAL SECTION

Discharge Apparatus

A Pyrex apparatus of the type shown in Figure 1 was used to generate a mixture of oxygen fluoride. Light yellow O_2F_2 was prepared in the discharge apparatus cooled to -196°C under relatively harsh conditions (4-5 kV at 20 ma) for about 1 hr. using a 2:1 fluorine to oxygen mixture. These conditions favor the production of O_2F_2. [28] After removal of unreacted O_2 and F_2 at -196°C by pumping to 10^{-5} torr, O_2F_2 was transferred to reaction tube A or C (Figure 1) by distillation through the apparatus. To minimize decomposition, all surfaces were pre-

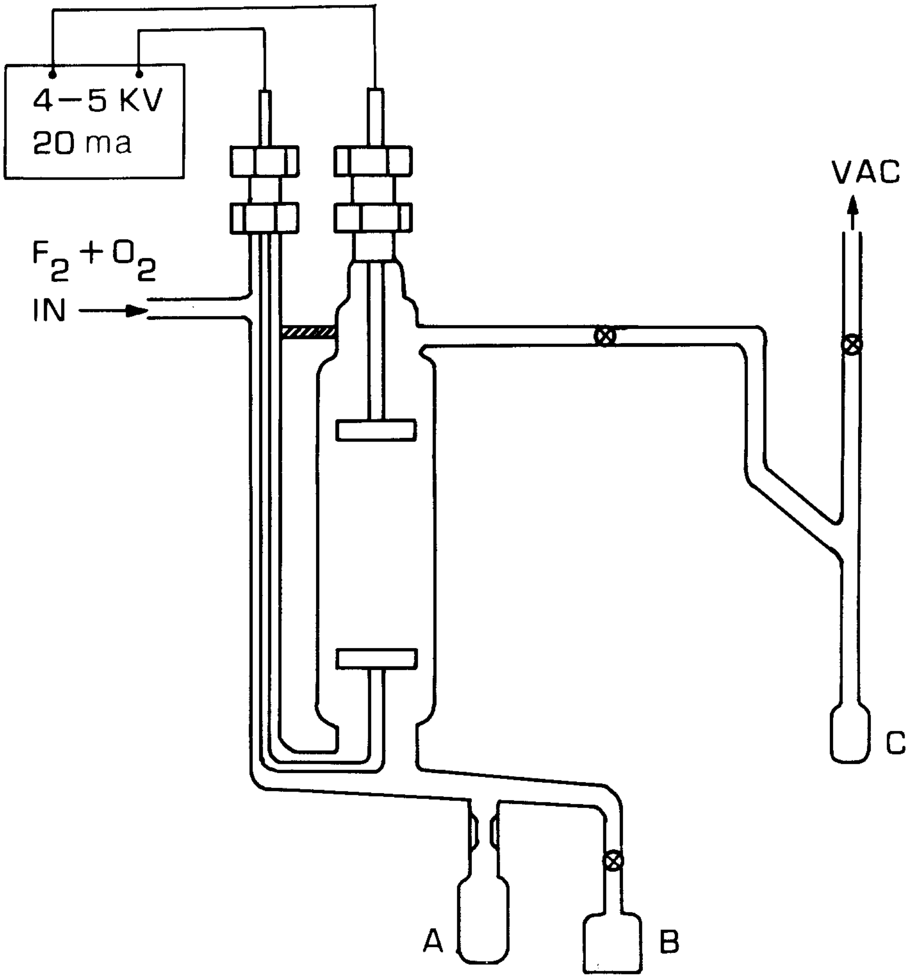

Figure 1. Pyrex discharge apparatus for low temperature syntheses. Quartz tube, 22 cm long x 6.3 cm diameter. Copper electrodes are 0.5 cm thick x 1.9 cm diameter and 7.5 cm separation. Electrical feedthroughs are Swagelock with brass bodies, teflon front and nylon rear ferrules. Valves are Monel with Teflon tips except for a Fischer-Porter Teflon and glass stopcock used to attach the apparatus to the vacuum system.

cooled by glass-wool insulation impregnated with liquid nitrogen or dry ice. After transfer of O_2F_2 to A or C, the solid was pale yellow with no trace of red material previously characterized as other oxide fluorides.[28] A sample sealed into C was examined using Raman methods and was found to be O_2F_2 with only a trace of $(\cdot O_2F)_n$ present as an impurity (vide infra).

Reaction of O_2F_2 with VF_5

Vanadium pentafluoride, contained in monel can B (Figure 1), was sublimed into glass sample tube C. Excess O_2F_2, prepared in the discharge tube, was also distilled into C through the pre-cooled apparatus and any O_2 and F_2 formed during the transfer was pumped away. The reaction was allowed to proceed at -160°C for one hour, at -109°C for 1 hour and finally at -78°C for 40 minutes. Unreacted O_2F_2 and any O_2 and F_2 were removed by pumping at -78°C before sealing off the reaction tube. The sample was stored at -196°C until it could be examined using Raman techniques.

Preparations of KVF_6, $CsVF_6$, KV_2F_{11} and CsV_2F_{11}

Weighed amounts of CsF or KF (∿ 0.25 gm) were loaded into openable monel reactors in the dry box and after evacuation the samples were conditioned with fluorine gas at 1 atmosphere pressure for 30 minutes. After removal of fluorine, excess VF_5 was sublimed into the reactor and the contents were allowed to stand for several hours. Removal of excess VF_5 by vacuum pumping at room temperature left involatile white products, which were subsequently identified by weight gain of vanadium pentafluoride (e.g. $VF_5/CsF = 1.97$, calculated for $CsV_2F_{11} = 1.92$ and $CsV_3F_{16} = 2.88$) and by their Raman spectra as CsV_2F_{11} or KV_2F_{11}. To remove one molecular unit of VF_5 from these products to produce $CsVF_6$ or KVF_6, the samples were heated to 80° while pumping under vacuum for several hours or until no further elimination of volatile material occured. The resulting products, $CsVF_6$ and KVF_6, showed no Raman bands due to the $V_2F_{11}^-$ anion. All products were white or slightly off-white in color.

Raman Spectra

Products of the $O_2F_2 + VF_5$ reaction were held in pencil or bulb shaped Pyrex sample tubes. Normally the products were formed on the walls of the lower parts of the tubes and could be examined with no further manipulation or contamination from outside sources. The experimental configuration for exciting, cooling and spinning the sample is shown in Figure 2. Temperatures from -155 to 25°C could be maintained to within $\pm$ 0.5°C at any temperature within this range by controlling the flow rate of the precooled nitrogen gas through the apparatus. Temperatures were measured with a Cu-Constantin thermocouple. For measurements at -196°C, the clear dewar was filled with liquid nitrogen.

Stable solids such as the cesium and potassium salts were examined in a previously described rotating cell assembly [18] at room temperature.

Raman spectra were measured with a Jarrel-Ash Model 25-100 double monochromator, a cooled RCA C31034 photomultiplier tube and a SSR photon count rate detector system. Samples were irradiated using Spectra Physics Model 164 Argon and Krypton lasers (5145 and 6471A).

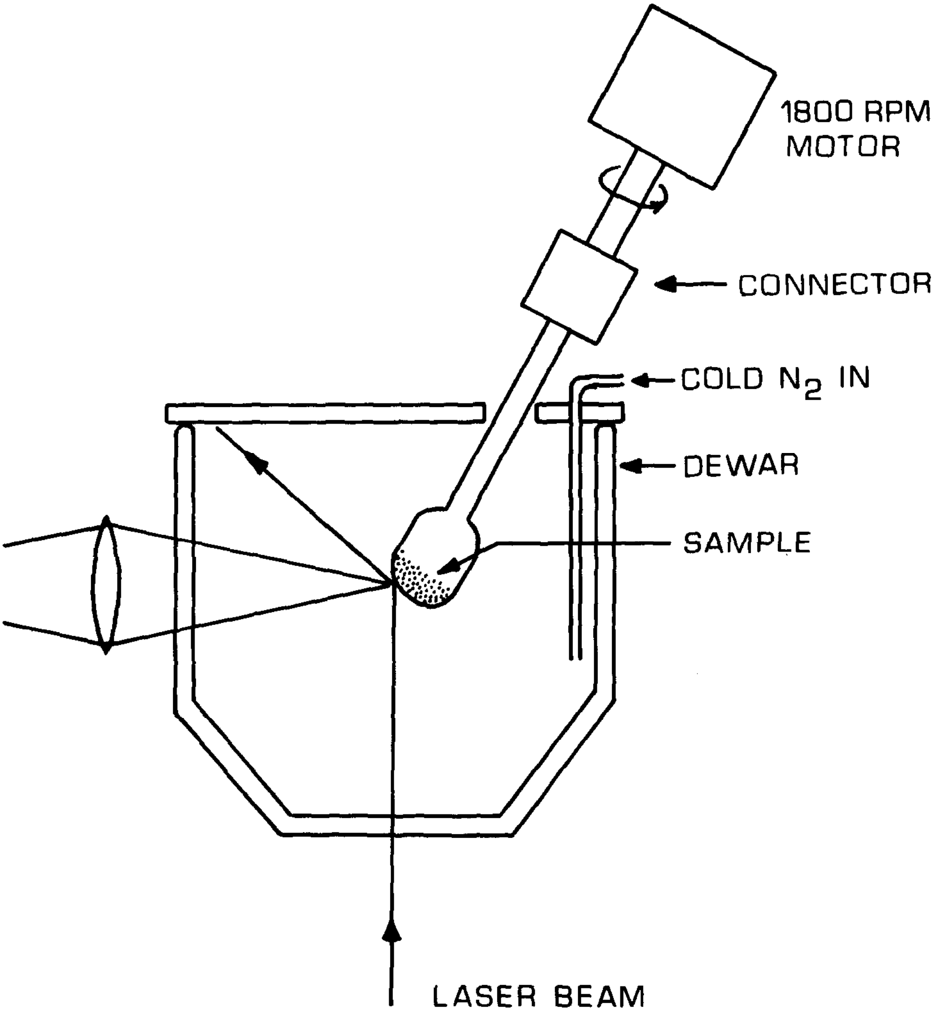

Figure 2. Low temperature Raman scattering apparatus for reactive species.

RESULTS AND DISCUSSION

The reaction of O_2F_2 with polymeric VF_5 is not simple. The thermal instability both of O_2F_2 and of the reaction product complicates elucidation of the overall process.

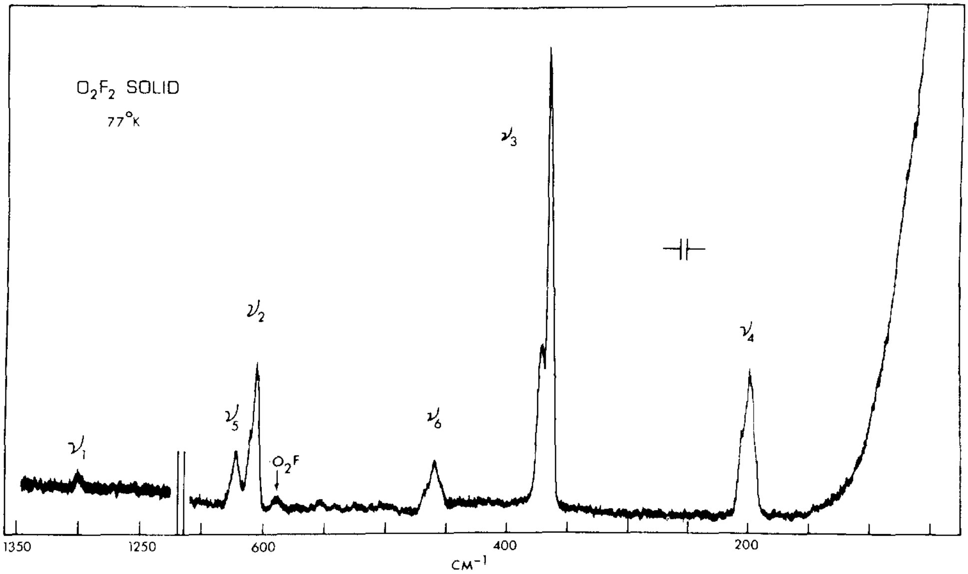

Figure 3. Raman spectrum of solid O_2F_2. Laser power = 0.8W (6471 A); spectral slit width = 4 cm^{-1}; scan rate = 50 cm^{-1}/min; time constant = 0.1 sec; sensitivity = 10^4 c/s full scale.

Raman spectroscopy was chosen to probe the intricacies of the reaction largely because the starting materials, the products and the reactive intermediates, each of which have properties that are temperature sensitive, could be well characterized using this technique. The ability to examine the various species in situ was a considerable advantage. The Raman

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Figure 4. Raman spectra of the products formed in the reaction of O_2F_2 with VF_5 at various temperatures. Spectra of VF_5(A), KVF_6(I) and KV_2F_{11}(J) are also shown. Experimental conditions are comparable to that for Figure 3. * intermediate species, ● plasma lines.

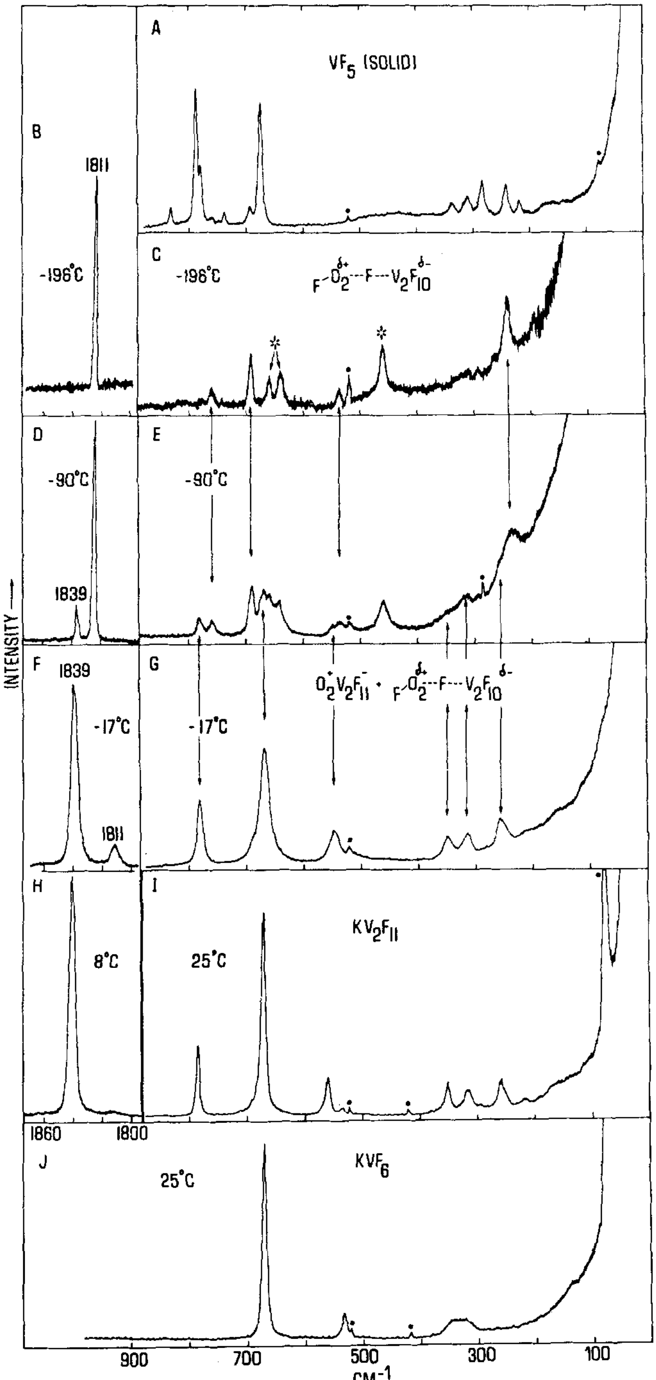

Figure 4. See opposite.

spectra of O_2F_2, solid VF_5, KV_2F_{11} and KVF_6 are shown in Figures 3, 4A, 4I and 4J; some of the numerical data are presented in Tables I-IV. The spectra of the reaction intermediates and products are shown in Figures 4 B-H and are discussed after the spectra of the reference compounds.

Dioxygenyl Difluoride

This molecule belongs to the point group C_2 and the irreducible representation of internal motion is $\Gamma(C_2) = 4A + 2B$ where all fundamentals are infrared and Raman active.

TABLE I

Fundamental Frequencies of Solid O_2F_2 (77°K).

Mode	This work	cm^{-1} ref. 24[a]	ref. 26[b]	Assignment[c]
1	1300(2)	1305	1306	O-O stretch
2	606(25) 611(11)	614 618	621	sym. O-F stretch
3	363(83) 371(27)	370	369	sym. O-O deformation
4	198(26) 205(12)	195	205	torsion
5	623(9)	630	615	asym. O-F stretch
6	460(8)	468	457	asym. O-O-F deformation

a. Raman values except for ν_4 which is an infrared solution value (ref. 24).

b. Infrared values (ref. 26).

c. Assignment to a particular well defined motion is made for clarity only. Normal coordinates are linear combinations of the symmetry coordinates. Mixing will be most prevalent between ν_2, ν_3, and ν_4 and between ν_5 and ν_6.

The spectrum, in Figure 3, shows that the A species exhibit a common feature which helps in the vibrational assignment. With the exception of the O-O stretching fundamental ν_1, which is too weak to show the effect clearly, the A modes are split; this probably reflects solid state effects. No well defined lattice modes were observed, however. Only a barely detectable trace of $(\cdot O_2F)_n$ could be identified ($\Delta\nu$ = 588 cm^{-1}). Our assignments, given in Table I, agree with those of Gardiner et al.[24] although the absolute values of the Raman shifts for the solid differ slightly from those given in the earlier work. We confirm the ν_2 = 606 and ν_5 = 623 cm^{-1} assignments, and observe directly the torsional fundamental ν_4 at 198 cm^{-1}. The solution value is 195 cm^{-1}.[24]

The KVF_6, $CsVF_6$, KV_2F_{11} and CsV_2F_{11} Salts

Octahedral anions of point group O_h generally exhibit simple spectra, $\Gamma(O_h) = A_{1g}(R) + E_g(R) + 2F_{1u}(IR) + F_{2g}(R) + F_{2u}$ (inactive) where R and IR denote Raman and infrared activity respectively. Thus a simple three line Raman spectrum is expected for VF_6^- although the E_g and F_{2g} bands may be split because of reduced site symmetry in the solid phase. The spectrum shown for KVF_6 in Figure 4J and the data in Table II confirm these expectations.

Neither the point group nor the site group of the $V_2F_{11}^-$ anions is known and therefore a credible assignment of the observed bands to fundamental modes of vibration cannot be made. Instead we have divided the observed Raman

TABLE II

Vibrational Frequencies of Fluoro Vanadium Anions[a]

KVF_6[b]	$CsVF_6$	KV_2F_{11}	CsV_2F_{11}	Assignment[c]
-	-	784(34)	759(40)	$\nu(V_2F_{11}^-)$
-	-	-	715(5)	$\nu(V_2F_{11}^-)$
-	-	671(100)	667(100)	$\nu(V_2F_{11}^-)$
670(100)	665(100)	-	-	$\nu_1(VF_6^-)$
-	-	558(19)	568(28)	$\nu(V_2F_{11}^-)$
-	-	534(3)	544(2)	$\nu(V_2F_{11}^-)$
532(13)	529(20)	-	-	$\nu_2(VF_6^-)$
342(10)	340(13)	-	-	$\nu_5(VF_6^-)$
322(10)	312(7)	-	-	$\nu_5(VF_6^-)$
-	-	351(17)	347(12)	$\delta(V_2F_{11}^-)$
-	-	-	323(5)	$\delta(V_2F_{11}^-)$
-	-	315(12)	313(18)	$\delta(V_2F_{11}^-)$
-	-	295(3)	285(3)	$\delta(V_2F_{11}^-)$
-	-	258(16)	261(28)	$\delta(V_2F_{11}^-)$
-	-	216(4)	208(2)br.	$\delta(V_2F_{11}^-)$
-	-	165(3)br.	151(8)	$\delta(V_2F_{11}^-)$

a. Values in parentheses are peak intensities based on the most intense band being equal to 100. Frequencies are in cm^{-1}.

b. Previous values (ref. 31) are $\nu_1 = 674$, $\nu_2 = 530$, $\nu_5 = 315$ cm^{-1}.

c. ν = stretching vibration; δ = deformation vibration for the $V_2F_{11}^-$ species.

bands into two types depending upon their frequency range. Those having values greater than 450 cm^{-1} were attributed to V-F stretching fundamentals and those having Raman shifts significantly lower were assigned as deformation modes. The data in Table II for KV_2F_{11} and CsV_2F_{11} are quite similar and characterize the anionic species adequately for subsequent use in determining the anion formed in the reaction of O_2F_2 with VF_5. There is one noticeable difference in the range of the highest frequency Raman bands for each anion. For the potassium and cesium salts, the difference in frequency is 25 cm^{-1} (Table II). The relative intensities are comparable and we have noticed that the spectra of the $V_2F_{11}^-$ anions are qualitatively similar to the spectra of other related $M_2F_{11}^-$ species.[18]

Reaction of O_2F_2 with VF_5

Solid VF_5 is a long chain fluorine bridged polymer in which most of the vanadium atoms are surrounded octahedrally by fluorine atoms.[29] This should result in a fairly complex Raman spectrum and the curve in Figure 4A is consistent with this. When O_2F_2 is allowed to react with VF_5 at -119°C for about 1 hour before quenching by cooling at -196°C several changes occur. Rather than present the observations first and explain them later, it is expedient to present first a mechanism of the reaction followed by the experimental evidence to support these speculations.

The following sequence is proposed: one fluorine atom in each O_2F_2 molecule interacts with the VF_5 polymer chain causing chain cleavage thereby producing smaller units of V_2F_{10} according to the first step shown in Figure 5. The reaction intermediate however does not include a $V_2F_{11}^-$ anion and therefore is formulated as $F\text{-}O\underline{\cdots}O^{\delta+}\cdots F^{\delta-}\cdots V_2F_{10}$ where δ has

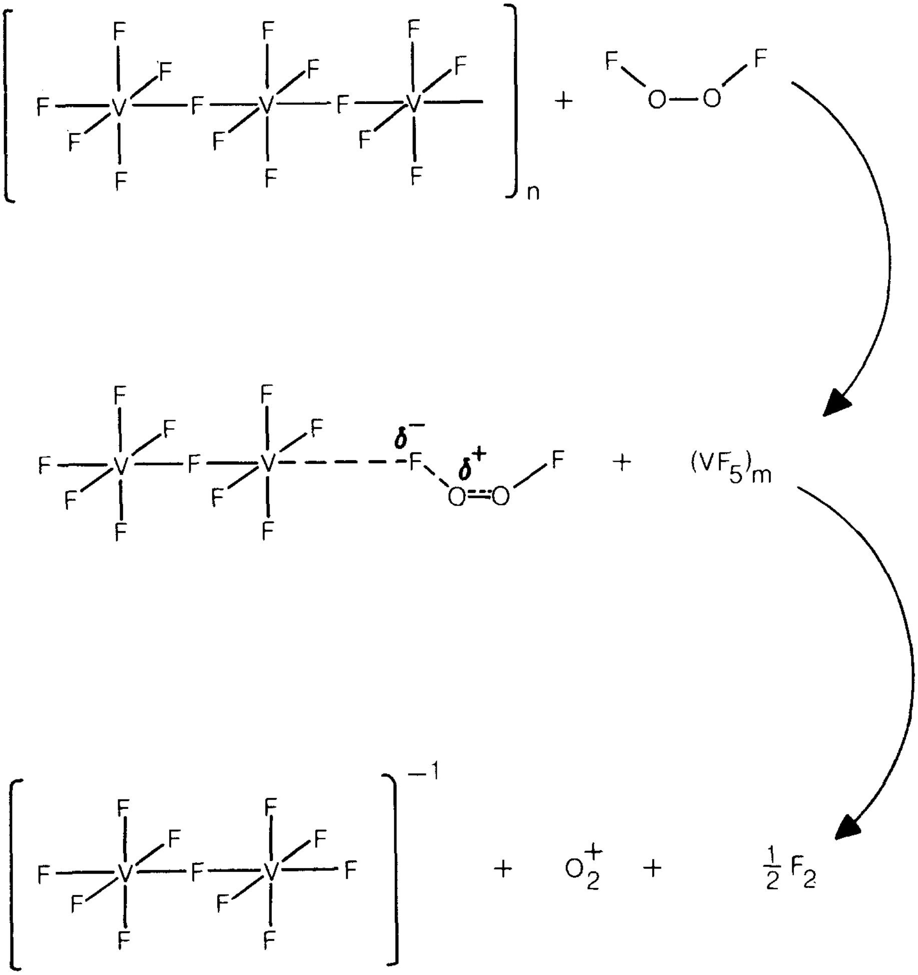

Figure 5. The reaction of O_2F_2 with VF_5 at low temperatures.

a value close to unity. With increasing temperature, the negatively charged fluorine atom from $F\text{-}O\,\underline{\cdot\cdot}\,O^{\delta+}\cdot F^{\delta-}\cdot\cdot$ attaches to the V_2F_{10} unit forming $V_2F_{11}^-$; simultaneously the other fluorine atom is eliminated leaving O_2^+ as the cation. Simultaneously is used in a generic sense and is not meant to define the time scale precisely.

Alternatively, the interaction could proceed with elimination of the first fluorine atom as a F^- ion leaving O_2F^+ as a well defined cation. A $V_2F_{11}^-$ ion still does not form in this first step, however; only chain cleavage to form V_2F_{10} units must occur. At higher temperatures, expansion of the lattice allows the F^- ion to attach itself to the strong fluoride ion acceptor V_2F_{10} forming a $V_2F_{11}^-$ anion. Increasing temperature also favors the process,

$$O_2F^+ \rightarrow O_2^+ + \cdot F \qquad (1)$$

$$2F\cdot \rightarrow F_2 \qquad (2)$$

Thus the overall process involves the formation of the reactive intermediate $F\text{-}O\underline{\cdots}O^{\delta+}\cdots F^{\delta-}\cdots V_2F_{10}$ or $O_2F^+ + F^- + V_2F_{10}$ which subsequently forms $O_2V_2F_{11} + \frac{1}{2}F_2$.

To assess these proposed reaction sequences, consider what changes would occur in the Raman spectra of the O_2F_2 and $(VF_5)_n$ species if these processes were in fact to proceed. Consider first,

$$O_2F_2 \rightarrow F\text{-}O\underline{\cdots}O^{\delta+}\cdots F^{\delta-}\cdot \qquad (3)$$

and

$$O_2F_2 \rightarrow O_2F^+ + F^- \qquad (4)$$

For process (3), the six line spectrum of O_2F_2 would reduce to a spectrum of three to six lines depending on the value of δ and on the residual $O^{\delta+}\cdots F^{\delta-}$ interaction. For $\delta = 1$, reaction (3) is equivalent to reaction (4) and only three Raman lines are expected for the triatomic O_2F^+ cation.

TABLE III

Fundamental Vibration Frequencies

Species	Fundamentals ν_1	ν_2	ν_3	State	Reference[a]
NOF	1844	521	766	Gas	32
O_2F^+	1811	460	642	Solid	This work[a]
$\cdot O_2F$	1520	376	582	Solid	27
NO^+	2232			Solid	18,19
NO	1876			Gas	33
O_2^+	1839[b]			Solid	This work
O_2	1555			Gas	34
O_2^-	1097			Solid	35

a. See discussion in text relating to this species.

b. Values between 1819[5] and 1865 cm^{-1} depending on the anion.[10,12,18]

Noticeable frequency shifts should also occur for both reactions and it is possible to estimate the magnitudes of these changes. The frequencies of isoelectronic species such as O_2^+ and NO are similar. In sequences of the type $O_2^- \rightarrow O_2 \rightarrow O_2^+$, the vibrational frequencies increase significantly from 1097 cm^{-1} to 1839 cm^{-1} (Table III). Thus, in the sequence $\cdot O_2F \rightarrow O_2F^+ \rightarrow$ NOF, one might reasonably expect that the fundamental frequencies of O_2F^+ would be bracketed by those of $\cdot O_2F$ and NOF which is isoelectronic with O_2F^+. By analogy, one might also expect the ν(O-O) and ν(N-O) stretching frequencies in O_2F^+ and NOF respectively to be comparable in absolute value. Furthermore, the intensity of the O-O stretching fundamental in O_2F^+ would be expected to be much greater than the corresponding vibration in O_2F_2, the starting material. The appropriate frequency data are summarized in Table III. Similar arguments hold for reaction (3) except that one cannot make a prediction about the number of observed Raman bands except to note that as $\delta \to 1$, the number of bands $n \to 3$. As the $O^{\delta+}\cdots F^{\delta-}\cdots$ bond length increases, however, the torsion mode ν_4 will probably be the first to lose its identity as a physically meaningful symmetry coordinate.

The VF_5 polymer spectrum is also expected to change dramatically with the cleavage of the chain into smaller units. The spectra of the VF_6^- and $V_2F_{11}^-$ ions are available for comparison to see whether these well defined anions are formed initially or not. Also, the presence or absence of VF_6^- in the final product provides an important clue as to whether VF_5 was formed initially or not. No VF_6^- ions were observed at any stage of the experiment. Since O_2F_2 was present in large excess, it is unlikely that V_3F_{15}, V_3F_{16} or larger units were formed. In any case, a separate experiment with <u>excess</u> VF_5 showed that some polymeric VF_5 remains unchanged after the reaction.

Evidence supporting our proposed reaction sequence is given in Figure 4. For a reaction temperature of -119°C, a very narrow and intense Raman band at 1811 cm^{-1} (Figure 4B) is formed ($F-O\underline{\cdots}O\cdot\overset{+}{\cdot}\cdot F\cdot\overset{-}{\cdot}\cdot$ or O_2F^+) and simultaneously the O-O stretching vibration of the parent at 1300 cm^{-1} disappears. The intensity of the 1811 cm^{-1} band decreases and another at 1839 cm^{-1} (O_2^+) increases as the temperature rises to -90°C (Figure 4D). This inverse temperature-intensity relationship continues (Figure 4F, -17°C) until at 8°C the 1811 cm^{-1} band has essentially vanished. The above sequence is irreversible with temperature thereby precluding an equilibrium or phase change interpretation. Concommitant with the high frequency behavior is the observation in Figure 4C, representing the first stage of the reaction, that polymeric VF_5, anionic VF_6^- or $V_2F_{11}^-$ and molecular O_2F_2 are absent (cf. Figs. 4A, 4J, 4I and 3 respectively). Instead, the intensities of a number of Raman bands at 762, 693, 538 and 242 cm^{-1}, tentatively attributed to the V_2F_{10} units, and at 661, 642 and 460 cm^{-1}, tentatively attributed to the $F{-}O\underline{\ldots}O^{\delta+}\cdot F^{\delta-}\cdot$ or O_2F^+ units, all decrease with increasing temperature in parallel with the band at 1811 cm^{-1}. Simultaneously, the intensities of Raman bands clearly identifiable with those found in the spectrum of KV_2F_{11} (Figure 4J) all increase just like the band found at 1839 cm^{-1} due to the O_2^+ ion. It is quite unambiguous that the O_2^+ and $V_2F_{11}^-$ ions are formed simultaneously from intermediate species. Identification of the anion is facilitated by frequency and relative intensity data given in Table IV. Monomeric VF_5 is not one of the intermediate species because of the absence of any VF_6^- in the final product. Units such as V_3F_{15} are also eliminated using similar reasoning. This leaves as choices of intermediates, $O_2F+ + F^- + V_2F_{10}$ or $F{-}O\underline{\ldots}O^{\delta+}\cdot F^{\delta-}\cdot V_2F_{10}$. If $\delta = 1$ there is no difference between the two,

Frequency arguments with respect to the 1811 cm^{-1} band slightly favor a well defined O_2F^+ cation with $\delta = 1$ but consideration of other bands in the spectra is not quite so convincing. For example, if the bands at 1811, 661, 642 and 460 cm^{-1} in Figure 4C are attributed to the oxygen fluoride species and the balance to the V_2F_{10} species,

TABLE IV

Vibrational Frequencies (cm^{-1}) of V-F Compounds

$FO_2^{\delta+}\cdots F^{\delta-}\cdots V_2F_{10}$	$O_2V_2F_{11}$	KV_2F_{11}	Assignment
-	1839	-	$\nu(O_2^+)$
1811(100)	-	-	$\nu(FO_2^+\cdots F^-)$
-	782(53)	784(34)	$\nu(V_2F_{11}^-)$
762(10)	-	-	$\nu(F^{\delta-}\cdots V_2F_{10})$
693(31)	-	-	$\nu(F^{\delta-}\cdots V_2F_{10})$
-	669(75)	671(100)	$\nu(V_2F_{11}^-)$
661(19)	-	-	$\nu(FO_2^{\delta+}\cdots F^{\delta-})$
642(22)	-	-	$\nu(FO_2^{\delta+}\cdots F^{\delta-})$
-	549(22)	558(19)	$\nu(V_2F_{11}^-)$
-	-	534(3)	$\nu(V_2F_{11}^-)$
538(11)	-	-	$\nu(F^{\delta-}\cdots V_2F_{10})$
460(31)	-	-	$\nu(FO_2^{\delta+}\cdots F^{\delta-}\cdots)$
-	350(18)	351(17)	$\delta(V_2F_{11}^-)$
-	315(17)	315(12)	$\delta(V_2F_{11}^-)$
-	-	295(3)	$\delta(V_2F_{11}^-)$
-	257(22)	258(16)	$\delta(V_2F_{11}^-)$
242(36)	-	-	$\delta(\cdots F^{\delta-}\cdots V_2F_{10})$
-	-	216(4)	$\delta(V_2F_{11}^-)$
-	-	165(3)	$\delta(V_2F_{11}^-)$

Intensities in parentheses are relative to the strongest band equal to 100.

the cationic moiety must be more complicated than O_2F^+ or $\delta < 1$. From the relative intensities of the various observed bands and taking account of the above assignments, the bands at 661 and 642 cm^{-1} should both be absent in Figure 4G if they are due to the more complicated oxygen fluoride species. If the species were O_2F^+, then only one of them would be due to the O_2F^+ species and one should correlate with the strong band at 693 cm^{-1} (Figs. 4C, E and G). Since both are undetected in Figure 4G, there is some evidence for $\delta < 1$. For a quasi tetra-atomic species, the number of observed bands n should be $3 \leq n \leq 6$, depending on how strongly bonded the labile fluorine atom is. For a loosely bound fluorine, the 0-0 bond would be very strong and hence $\nu(0\text{-}0)$ would be high, as observed. Also, the torsion mode would be the least well defined symmetry coordinate. Experimentally, only an extremely weak Raman intensity can be detected near 200 cm^{-1} (Figure 4C) in contrast to the intense torsion mode ν_4 observed for O_2F_2 in Figure 3. Of the remaining four fundamentals of O_2F_2 between 350 and 650 cm^{-1}, only three are clearly observed in Figure 4C and it is unduly speculative to try to assign these to normal modes of a species that is already a speculation. Much of the foregoing argument really rests upon the tacit assumption that both bands, 661 and 642 cm^{-1}, are due to the oxygen fluoride cationic species and this point has already been discussed. A definitive answer to whether $\delta = 1$ or say $\delta = 0.92$ is nebulous at best on the basis of the available evidence. It is clear that better experiments are needed to provide an unambiguous solution. Nevertheless, the important point is that reactive intermediates have been isolated and characterized. The data also cast some light on earlier work with O_2F_2 and strong fluoride ion acceptors.

It is worth noting that the processes,

$$O_2F_2 \rightarrow \cdot O_2F + \cdot F$$

$$\cdot F + \cdot F \rightarrow F_2$$

$$\cdot O_2F + BF_3 \rightarrow O_2FBF_3$$

$$O_2FBF_3 \rightarrow O_2^+BF_4^-$$

have been proposed [15] as important steps in the reaction to produce $O_2^+BF_4^-$. In the present closely related work no evidence for the well known $\cdot O_2F$ free radical was found. Rather, the evidence strongly favors an ionic type intermediate. The 0-0 stretching frequency of $\cdot O_2F$ is near 1520 cm^{-1} [27] and not at 1811 cm^{-1}. In the present work care was taken to minimize the concentration of $\cdot O_2F$.

Although $\cdot O_2F$ seems to be eliminated as an important species in the reaction leading ultimately to the new compound $O_2^+V_2F_{11}^-$, details of the mechanism still need further clarification. For example, is the second fluorine atom in the quasi cation FO_2^+ the one that is eliminated as molecular fluorine or not? Also, will the ionic reactive intermediates of the type described here be important species in a variety of related syntheses? These are important considerations and work in progress may lead to answers to these questions.

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