

Table V. Activation Parameters for the Oxidation of Some Oxy Acids of Group 5B Elements by Vanadium(V)^a

Substrate	Medium	No. of electrons transferred	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , cal/(mol deg)
H ₃ PO ₂ ¹⁰	H ₂ SO ₄	1	18.95	-5.1
H ₃ PO ₂ ¹⁰	HClO ₄	1	18.8	-5.7
H ₃ PO ₃ ¹²	H ₂ SO ₄	1	22.9	-6.9
H ₃ PO ₃ ¹²	HClO ₄	1	20.4	-15.2
C ₆ H ₅ PO ₂ H ₂ ¹¹	H ₂ SO ₄	1	28.8	15.3
C ₆ H ₅ PO ₂ H ₂ ¹¹	HClO ₄	2	12.2	-36.9
As ₂ O ₃ ⁹	H ₂ SO ₄	2	5.7	-50.8
As ₂ O ₃ ⁹	HClO ₄	2	7.6	-48.2
Sb ₂ O ₃	H ₂ SO ₄	2	11.3	-32.7
Sb ₂ O ₃	HClO ₄	2	8.5	-43.6

^a The polymerization test was applied in all of these cases, and in all of these one-electron-transfer reactions the addition of acrylamide yielded positive test.

a great tendency to hydrolyze²¹ and cationic compounds of antimony(III) exist as the so-called "antimonyl" ion, SbO⁺, and not as HSbO₂. Again, the increase in rate in acetic acid is so pronounced (unlike that in sulfuric and perchloric acid media) that the changes may be considered mainly due to changes in dielectric constant, and the positive slope of the plot of logarithm of the second-order rate constant against the reciprocal of the dielectric constant indicates that one of the reactive species is positively charged. The species^{1,9-12} of vanadium(V) like V(OH)₃HSO₄⁺ and V(OH)₃²⁺, which participate in many vanadium(V) oxidations, cannot be considered as the other reacting species in sulfuric and perchloric acids, respectively since the addition of perchlorate, bisulfate, or sulfate to the reaction mixture failed to alter the rate of reaction. The second-order dependence on mineral acids may be explained assuming (VO₂·2H₂SO₄)⁺ and V(OH)₂³⁺ as the reactive species for the respective cases of oxidation. However, the removal of a single electron from antimony(III) must result in the formation of a free-radical intermediate if vanadium(V) behaves as a one-electron-transfer oxidant. It is to be mentioned that neither has the antimony(IV) compound been isolated in the free state nor has its existence been established from spectral measurement.^{22,23} The addition of acrylamide to the reaction mixture failed to cause polymerization, suggesting that free radicals do not intervene in the oxidation-reduction reaction. Consequently, vanadium(V) may behave as a two-electron oxidant. Again, the kinetic evidence points to a transition state having vanadium(V), antimony(III) (possibly HSbO₂), two protons, and an unknown number of solvent molecules. The reactive species of vanadium(V) would therefore react with antimony(III) leading to the oxidation of the same to antimony(V). Vanadium(III) which is produced in the slowest step would further react with vanadium(V) producing 2 mol of vanadium(IV). The reaction between vanadium(III) and vanadium(V) is very fast.³

Although the slowest steps have been explained by a two-electron-transfer mechanism, an alternative path assuming vanadium(V) as a one-electron-transfer oxidant cannot be totally ruled out. In the oxidation of hydrazine by vanadium(V), Higginson et al.² have suggested that vanadium(V) behaves as both a 1- and 2-equiv oxidant. However, in an oxidation-reduction reaction between an ion of a transition element and a compound or ion derived from a nontransition element, the formation of a free radical or unstable oxidation state from the second reactant by a 1-equiv reaction is likely in some cases to be a more endothermic process than the corresponding 2-equiv reaction.²⁴ The exothermic process is able to lower the activation energy of reaction below that of the corresponding one-electron process.² The heats as well as entropies of activation are smaller than those obtained in

previous studies¹⁰⁻¹² where vanadium(V) behaves as a 1-equiv oxidant. The smaller activation parameters obtained in the present study lend further support to the view that vanadium(V) behaves as a 2-equiv oxidant. Corroborative evidences come from similar investigations concerning the oxidations of arsenic(III)⁹ and benzenephosphonous acid¹¹ by vanadium(V). These reactions where vanadium(V) behaves as a 2-equiv oxidant are also characterized by low activation parameters unlike the values which have been obtained in the oxidations of hypophosphorous¹⁰ and phosphorous acids¹² by vanadium(V) where the oxidant behaves as a one-electron reagent. The results presented in Table V would therefore support the contention that vanadium(V) behaves as a two-electron and not as a one-electron oxidant in the present study.

Registry No. Sb(III), 23713-48-6; V(V), 22537-31-1.

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Hydrostatic Pressure Effects upon the Metal-Chlorine Stretching Vibrations of Some 4-Substituted Pyridine Complexes of Zinc Chloride¹

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The symmetric and antisymmetric Zn-Cl stretching frequencies of a series of tetrahedral complexes of the form [Zn(4-Rpy)₂Cl₂], where 4-Rpy are 4-substituted pyridine derivatives, have been measured by both far-infrared and Raman spectroscopies.^{2,3} Substituents on the fourth position of the pyridine rings shift the Zn-Cl stretching frequencies and their magnitude can be correlated with the electron-releasing and -withdrawing abilities of the substituents. These results have been interpreted in terms of the change of the Zn-Cl bond nature induced by the substituents.^{2a}

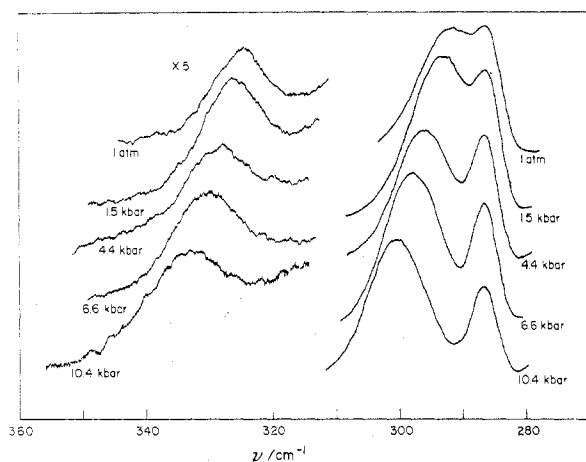


Figure 1. Raman spectra of the $[\text{Zn}(\text{py})_2\text{Cl}_2]$ complex in the frequency region of the Zn-Cl stretching modes at various pressures.

In the present work the Raman frequencies of the Zn-Cl modes of some zinc complexes $[\text{Zn}(4\text{-Rpy})_2\text{Cl}_2]$, where R is H, the electron-releasing group CH_3 , or the electron-withdrawing group CN, have been studied under hydrostatic pressure in the range 0–12 kbars in the hope of obtaining additional information about the effects of the substituents upon the nature of the Zn-Cl bonds.

The pressure effects upon the infrared bands of the symmetric and antisymmetric metal-halogen stretching modes of some complexes similar to those in the present work, i.e., 2,2',2''-terpyridinedichlorozinc(II), 2,2',2''-terpyridinedibromozinc(II), bis(pyridine)dibromocobalt(II), bis(α -picoline)dichlorocobalt(II), and bis(α -picoline)dibromocobalt(II), have been studied using opposed diamond anvils by Postmus, Nakomoto, and Ferraro,⁴ and no change in frequencies of these bands has been observed at pressure as high as ~ 40 kbars. We have found, however, a significant pressure dependence in our compounds.

Experimental Method

The preparation and the chemical analysis of the complexes have been reported elsewhere.⁵

The Raman spectra of the polycrystalline samples were recorded with a Jarrell-Ash Model 25-300 laser Raman spectrometer consisting of a Coherent Radiation Model 52 argon ion laser, a 25-100 Czerny-Turner double monochromator, and an ITT FW-130 photomultiplier tube and electron-pulse-counting readout system.

The high-pressure Raman cell used in the present study was constructed of nickel maraging steel.⁶ The pressure fluid was naphtha in which the sample was immersed and the pressure was measured to ± 0.1 kbar with a calibrated manganin gauge.

The 514.5-nm argon line at a power of ~ 1 W was used to illuminate the sample from the top and the Raman emission of the sample was collected at 90° to the incident laser beam. The spectral slit width was ~ 3 cm^{-1} and the scanning speed was 2 $\text{cm}^{-1} \text{min}^{-1}$.

As a standard for the frequency calibration, the line at $\Delta\nu = 286.9$ cm^{-1} from an Ultra-Violet Products, Inc., neon lamp was recorded during the course of the measurement for each spectrum, so that the maximum error of the frequency is ± 0.2 cm^{-1} for the symmetric and ± 0.3 cm^{-1} for the antisymmetric Zn-Cl stretching mode.

Results and Discussion

The crystal structure of all the three complexes in the present study is monoclinic with four molecules per unit cell and their molecular configuration is pseudotetrahedral.^{3,7,8} The Raman intensity of the antisymmetric Zn-Cl stretching mode is weak and is about a factor of 8 weaker than the symmetric mode.^{2b,3} Typical spectra for the $[\text{Zn}(\text{py})_2\text{Cl}_2]$ complex at various pressures are shown in Figure 1. The band at 286.9 cm^{-1} is due to the neon emission which was used for the frequency calibration. The weak band at ~ 330 cm^{-1} was recorded with

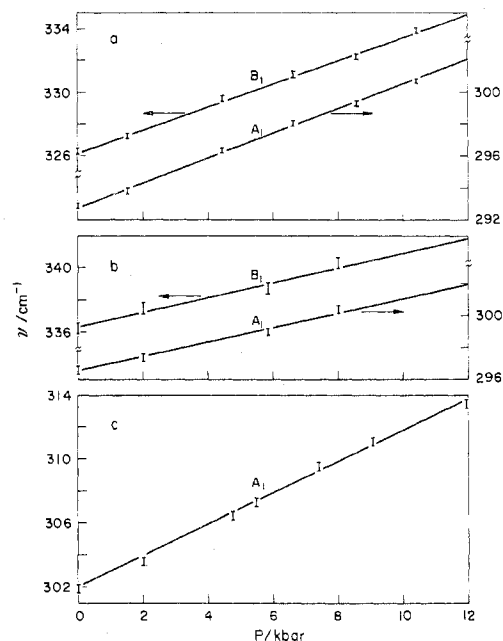


Figure 2. Pressure dependences of the symmetric (A_1) and antisymmetric (B_1) Zn-Cl stretching modes of $[\text{Zn}(\text{py})_2\text{Cl}_2]$ (a), $[\text{Zn}(4\text{-CNpy})_2\text{Cl}_2]$ (b), and $[\text{Zn}(4\text{-CH}_3\text{py})_2\text{Cl}_2]$ (c) complexes.

Table I. Frequencies and Pressure Dependences of the Symmetric (A_1) and Antisymmetric (B_1) Zn-Cl Stretching Modes

Complex	A_1 mode		B_1 mode	
	ν , cm^{-1}	$d\nu/dP$, $\text{cm}^{-1} \text{kbar}^{-1}$	ν , cm^{-1}	$d\nu/dP$, $\text{cm}^{-1} \text{kbar}^{-1}$
$[\text{Zn}(4\text{-CNpy})_2\text{Cl}_2]$	296.6	0.47	336.2	0.48
$[\text{Zn}(\text{py})_2\text{Cl}_2]$	292.9	0.76	326.3	0.73
$[\text{Zn}(4\text{-CH}_3\text{py})_2\text{Cl}_2]$	301.9	0.99		

the counting rate decreased by a factor of 5. The pressure dependences of the frequencies of the complexes $[\text{Zn}(\text{py})_2\text{Cl}_2]$, $[\text{Zn}(4\text{-CNpy})_2\text{Cl}_2]$, and $[\text{Zn}(4\text{-CH}_3\text{py})_2\text{Cl}_2]$ are shown in Figure 2. Some fluorescence occurred near the antisymmetric Zn-Cl stretching mode for the $[\text{Zn}(4\text{-CH}_3\text{py})_2\text{Cl}_2]$ complex and the frequency of this weak band was difficult to measure accurately, so its pressure dependence was not measured. Several spectra were recorded at each pressure and the bar of each point in Figure 2 indicates the standard deviation from the least-squares fit. The numerical values of the frequencies and the pressure coefficients are listed in Table I.

The frequencies are strongly pressure dependent and increase approximately linearly with pressure. In the case of the $[\text{Zn}(4\text{-CH}_3\text{py})_2\text{Cl}_2]$ complex the frequency shift is as large as 0.99 $\text{cm}^{-1} \text{kbar}^{-1}$, which is comparable to or even larger than that of the lattice modes of most of the ionic and molecular crystals reported in the literature (see for example, ref 9–11 and the references cited therein).

The pressure effect on the Zn-Cl stretching frequencies is strongly affected by the functional group R. As shown in Table I, the electron-releasing group CH_3 enhances the pressure shift of the frequencies, whereas the electron-withdrawing group CN reduces it. Since both the crystal structures and the molecular configurations of the three complexes are essentially the same, the force exerted on the Zn-Cl bonds at a constant hydrostatic pressure should be the same. Therefore the difference in the pressure effect upon the Zn-Cl stretching frequencies among these three complexes is due to differential characteristics of the Zn-Cl bonds in these three complexes.

It has been suggested^{2a,12} that the electron-releasing groups on the pyridine rings of the complex $[\text{Zn}(4\text{-Rpy})_2\text{Cl}_2]$ strengthen the $d\pi$ - $d\pi$ zinc to chlorine bonding. Electron-

withdrawing groups enhance the donation of electron density from the chlorine atoms to the zinc atom, so that the σ bonding between the chlorine and zinc atoms becomes stronger. Therefore the results of the present work indicate that the zinc to chlorine π bonding in the complexes $[\text{Zn}(4\text{-Rpy})_2\text{Cl}_2]$ is more sensitive to pressure than the σ bonding in the Zn-Cl bonds.

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Registry No. $[\text{Zn}(\text{py})_2\text{Cl}_2]$, 6843-20-5; $[\text{Zn}(4\text{-CH}_3\text{py})_2\text{Cl}_2]$, 13869-84-6; $[\text{Zn}(4\text{-CNpy})_2\text{Cl}_2]$, 19234-43-6.

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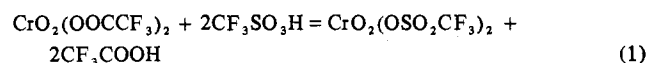
New Chromyl Compounds. II.¹ Reaction of Chromyl Trifluoroacetate with Strong Acids

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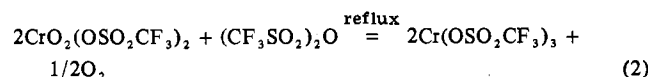
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Two new chromyl compounds, $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$ and $\text{CrO}_2\text{NO}_3(\text{OOCFF}_3)$, have been prepared and characterized. When chromyl trifluoroacetate reacts with trifluoromethanesulfonic acid, chromyl trifluoromethanesulfonate is formed in $\sim 100\%$ yield according to the equation



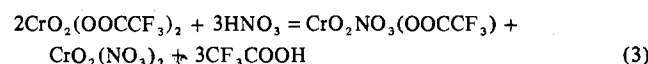
Chromyl trifluoromethanesulfonate is a mustard yellow crystalline solid which is extremely hygroscopic, fumes in the atmosphere, and reacts with a large excess of water to form a yellow chromate solution. The compound is soluble in CCl_4 and $\text{CF}_3\text{SO}_3\text{H}$.

In excess trifluoromethylsulfonyl anhydride, $(\text{CF}_3\text{SO}_2)_2\text{O}$, $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$ is reduced



$\text{Cr}(\text{SO}_3\text{CF}_3)_3$ is soluble in water, $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OH , and $(\text{CH}_3\text{CH}_2)_2\text{O}$ and is insoluble in CCl_4 .

With anhydrous nitric acid, chromyl trifluoroacetate yields a new mixed-chromyl compound



Chromyl nitrate trifluoroacetate is an amorphous deep red-brown solid which is easily hydrolyzed. It is the second

example of a mixed-ligand chromyl compound, the first being CrO_2ClF_2 .

Chromyl trifluoroacetate also reacts with fluorosulfuric acid (HSO_3F) according to the equation



Chromyl fluorosulfate has been reported previously.³

The infrared spectra for $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$ and $\text{Cr}(\text{OSO}_2\text{CF}_3)_3$ are more complex than one would expect if the SO_3CF_3 group were a monodentate ligand. The observed complexity is presumed to be caused by SO_3CF_3 groups of different functionality. For $\text{CrO}_2(\text{SO}_3\text{CF}_3)_2$ the bands at 1380 and 1220 cm^{-1} are interpreted as sulfur-oxygen stretching modes of a monodentate trifluoromethanesulfonate group primarily on the basis of their similarity to the corresponding bands for this group in $[\text{I}(\text{OSO}_2\text{CF}_3)_4]^-$ and $\text{I}(\text{OSO}_2\text{CF}_3)_3$.⁴

The bands at 1340, 1105, and 975 cm^{-1} for $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$ and the bands at 1352, 1100, and 995 cm^{-1} for $\text{Cr}(\text{OSO}_2\text{CF}_3)_3$ are similar in position to those found for the sulfur-oxygen stretching modes for a bidentate SO_3CF_3 group.⁴ The remaining bands for $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$, in this region, at 1220, 1155, and 1000 cm^{-1} may be attributed to CF_3 stretching modes. The bands at 937 and 912 cm^{-1} are attributable to the asymmetric and symmetric CrO stretching modes, respectively. In $\text{CrO}_2(\text{OSO}_2\text{CF}_3)_2$ the band at 385 cm^{-1} is assigned to the Cr-O deformation mode. Additional bands in the 400- cm^{-1} region are tentatively assigned to Cr-O deformation modes. The Cr-O deformation mode in CrO_2Cl_2 is located at 357 cm^{-1} and at 304 cm^{-1} in CrO_2F_2 .⁵

The infrared spectrum of $\text{CrO}_2\text{NO}_3(\text{OOCFF}_3)$ is more complex due to the overlapping of similar vibration bands for the NO_3 and CF_3COO groups. However, bands arising from both unidentate and bidentate nitrate groups appear to be present. We tentatively assign the bands at 1570 and 1365 cm^{-1} , respectively, to $\nu_{\text{asym}}(\text{NO}_2)$ and $\nu_{\text{sym}}(\text{NO}_2)$ of the unidentate nitrate group and the band at 1660 cm^{-1} to the $\nu(\text{NO})$ of the bidentate group. The band at 670 cm^{-1} in the nitrate-bending region is likely, by comparison with $\text{VO}(\text{NO}_3)_3$, to be associated with the symmetric deformation of the bidentate nitrate group and the band at 765 cm^{-1} is assigned to the symmetric deformation mode of the unidentate group. The bands at 450 and 370 cm^{-1} are probably due to vibrations of the metal-bidentate nitrate linkage. These assignments are also based on previous work with $\text{VO}(\text{NO}_3)_3$ ⁶ and $\text{VO}(\text{N-O}_3)_3 \cdot \text{CH}_3\text{CN}$.⁷ Additional bands attributable to the nitrate group occur at 1150 cm^{-1} ($\nu_{\text{sym}}(\text{NO}_2)$), 795 cm^{-1} ($\rho(\text{NO}_3)$), and 720 cm^{-1} ($\delta(\text{ONO})$).

The tentative assignments for the CF_3COO groups are 1772 cm^{-1} ($\nu_{\text{asym}}(\text{COO})$), 1660 cm^{-1} ($\nu_{\text{asym}}(\text{COO})$), 1470 cm^{-1} ($\nu_{\text{sym}}(\text{COO})$), 1430 cm^{-1} ($\nu_{\text{sym}}(\text{COO})$), 855 cm^{-1} (C-C), 720 cm^{-1} ($\delta(\text{COO})$), 645 cm^{-1} ($\delta(\text{CCO}_2)$), and 325 cm^{-1} ($\rho(\text{C-CF}_3)$). Of particular importance are the CF_3 deformation modes (620 + 530 cm^{-1}) which are located essentially at the same frequencies as found for $\text{Cu}(\text{CF}_3\text{COO})_2$ and $\text{Cu}(\text{py})_2(\text{CF}_3\text{COO})_2$.⁸ Since both of these copper compounds have bidentate attachment of the trifluoroacetate group, it is reasonably safe to assume that the CF_3COO groups in our compound show bidentate behavior as well.

The absorption band at 945 cm^{-1} is assigned to the asymmetric and symmetric stretching frequencies of the CrO_2 group. The presence of bridging nitrate and trifluoroacetate groups would explain the amorphous characteristics of $\text{CrO}_2\text{NO}_3(\text{OOCFF}_3)$.

The vibrational frequencies for the green form of $\text{CrO}_2(\text{SO}_3\text{F})_2$ which are due to the fluorosulfate group are located at 1350 cm^{-1} ($\nu(\text{SO})$), 1195 cm^{-1} ($\nu_{\text{asym}}(\text{SO}_2)$), 1050 cm^{-1} ($\nu_{\text{sym}}(\text{SO}_2)$), 810 cm^{-1} ($\nu(\text{SF})$), 618 cm^{-1} ($\rho(\text{SO})$), 575 cm^{-1} ($\delta(\text{SO}_2)$), 550 cm^{-1} ($\rho(\text{SO}_2)$), 450 cm^{-1} ($\rho(\text{SF})$), and 330 cm^{-1} (SO_2F torsion) and agree very closely with frequencies found