Journal of Fluorine Chemistry, 27 (1985) 133–142

Received: October 4, 1983; accepted February 3, 1984

VANADIUM (III), OXOVANADIUM (IV) AND OXOVANADIUM (V) TRIFLUOROMETHANESULFONATES

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SUMMARY

$V(SO_3CF_3)_3$, $VO(SO_3CF_3)_2$ and $VO(SO_3CF_3)_3$ have been prepared by reacting $V(O_2CCF_3)_3$, $VO(O_2CCF_3)_2$ and $VOCl_3$ with HSO_3CF_3. The i.r. data suggest a bridging bidentate nature for SO_3CF_3 groups. The diffuse reflectance spectrum of $V(SO_3CF_3)_3$ suggests hexacoordination of vanadium, whilst that of $VO(SO_3CF_3)_2$ is comparable to either five or six coordinated oxovanadium (IV) systems. The magnetic moments of $V(SO_3CF_3)_3$ and $VO(SO_3CF_3)_2$ are slightly lower than the spin-only values. Thermal decomposition of these triflates is simple. All the three triflates form coordination complexes with pyridine, 2, 2'-bipyridyl and triphenylphosphine oxide.

INTRODUCTION

Reports on the synthesis of vanadium (III), oxovanadium (IV) and oxovanadium (V) derivatives of strong organic and inorganic protonic acids extend well into the last century. More recent examples of this class of compounds include:

0022-1139/85/$3.30

$V(SO_3F)_3$ 1 , $VO(SO_3F)_2$ 2 , $VO(SO_3F)_3$ 3 , $V(SO_3CH_3)_3$ 4 , $VO(SO_3CH_3)_2$ 5 , $VO(SO_3F)_3$ 5 , $V(O_2CCF_3)_3$ 6 , and $VO(O_2CCF_3)_2$ 6 . Oxovanadium (V) trifluoroacetate is not known; instead $VO_2(O_2CCF_3)$ 6 appears to be formed. Preparation of $VO(SO_3CF_3)_3$ by a different route is reported 7 . Trifluoromethanesulfonic acid is one of the strongest acids, comparable in strength to fluorosulfuric acid 8 . The high acidity of HSO_3CF_3 implies very low basicity and weak coordinating ability of the SO_3CF_3 ion.

EXPERIMENTAL

Materials

Trifluoromethanesulfonic (Aldrich) and trifluoroacetic acids (B.D.H.) were distilled before use. Vanadium (III) chloride 9 , oxovanadium (IV) chloride 10 and oxovanadium (V) trichloride 11 were prepared according to literature methods. $V(O_2CCF_3)_3$ and $VO(O_2CCF_3)_2$ were prepared by refluxing VCl_3 and $VOCl_2$, respectively, with trifluoroacetic acid 6 . Pyridine (Py) and the solvents were purified as described in the literature 12 . Triphenylphosphine oxide (TPPO) (E. Merck) and 2,2'-bipyridyl (bipy) (B.D.H., A.R.) were used as such.

Vanadium (III) trifluoromethanesulfonate, $V(SO_3CF_3)_3$.(A)

A slight excess of CF_3SO_3H (3.34 g, 5.13 mmol) was added to (2.0 g, 5.13 mmol) of $V(O_2CCF_3)_3$ in 10 ml of trifluoroacetic acid. The reaction mixture was stirred magnetically for 8 h at room temperature under dry N_2. A greenish solution obtained was evaporated to dryness under vacuum. Finally, the green

solid was dried by heating at 90°C under vacuum, until a constant weight (2.548 g, 5.11 mmol of $V(SO_3CF_3)_3$ was obtained.

Oxovanadium (IV) trifluoromethanesulfonate, $VO(SO_3CF_3)_2$, (B)

Excess of CF_3SO_3H (23.77 g, 158.47 mmol) was added to (5.46 g, 18.63 mmol) of $VO(O_2CCF_3)_2$ in 10 ml of trifluoroacetic acid. The reaction mixture was stirred for 10 h at room temperature under dry N_2. A blue solid isolated was filtered under dry N_2 and repeatedly washed with CF_3CO_2H (5 ml containing one ml of CF_3SO_3H). 6.65 g, 18.22 mmol of $VO(SO_3CF_3)_2$ were obtained after removal of all volatiles under vacuum.

Oxovanadium (V) trifluoromethanesulfonate, $VO(SO_3CF_3)_3$, (C)

A slight excess of CF_3SO_3H (8.82 g, 58.8 mmol) was added to (2.55 g, 14.7 mmol) of $VOCl_3$. The reaction mixture was left overnight. A dark green solid appeared, accompanied by a slow evolution of HCl gas. The contents were further heated at reflux until evolution of HCl ceased. The volatiles were removed under vacuum and the remaining dark green solid was heated at 110°C under vacuum until constant weight (7.55 g, 14.68 mmol) was obtained.

Preparation of complexes

The complexes A.2Py, B.2Py, C.2Py, A.bipy, B.bipy, C.bipy, A.2TPPO, B.2TPPO and C.2TPPO were prepared by stirring a suspension of A, B or C in an appropriate solvent (CCl_4 for pyridine complexes and benzene for others) with the ligand in the required stoichiometry for about 20 h under dry N_2 at room temperature. The adducts formed were filtered under N_2, washed with the respective solvent and finally dried under vacuum. Complexes of the same stoichiometry were obtained even when the ligands used were in excess.

Analytical methods

Vanadium was determined as V_2O_5 gravimetrically after decomposing the complex with concentrated nitric acid and igniting the residue. Sulfur was determined as $BaSO_4$ after fusing the known weight of the complex with fusion mixture (Na_2O_2 and Na_2CO_3 in 1:2 ratio). Fluorine was determined as described 13 . Carbon, hydrogen and nitrogen were determined microanalytically. The analytical results are given in Table 1.

Physical measurements

The i.r. spectra of the compounds were recorded as Nujol and hexachlorobutadiene mulls between silver chloride plates using a Perkin-Elmer 621 spectrophotometer. Diffuse reflectance spectra of powdered complexes were recorded on a Unicam SP 735 spectrophotometer using freshly sublimed MgO as reference. Magnetic susceptibilities were determined at room temperature using Gouy's method. Thermal analysis was carried out by means of a Stanton thermobalance at a heating rate of 4°C/minute. All manipulations were carried out in a dry box filled with dry N_2.

RESULTS AND DISCUSSION

Trifluoromethanesulfonic acid reacts with $V(O_2CCF_3)_3$ and $VO(O_2CCF_3)_2$ exothermally at room temperature to give $V(SO_3CF_3)_3$ (eqn. 1) and $VO(SO_3CF_3)_2$ (eqn. 2) respectively. Reaction of CF_3SO_3H with $VOCl_3$ for about 12 h at room temperature and then under reflux for another 2 h resulted in the formation of $VO(SO_3CF_3)_3$ (eqn. 3).

TABLE 1

Analytical data

COMPOUND	Found (calc) %					
	V	S	F	C	H	N
$V(SO_3CF_3)_3$	10.1 (10.2)	19.6 (19.3)	34.1 (34.3)	7.1 (7.2)	-	-
$VO(SO_3CF_3)_2$	14.0 (14.0)	17.4 (17.5)	30.9 (31.2)	6.5 (6.6)	-	-
$VO(SO_3CF_3)_3$	9.7 (9.9)	18.8 (18.7)	32.8 (33.3)	6.8 (7.0)	-	-
$V(SO_3CF_3)_2.2Py$	7.7 (7.8)	14.6 (14.6)	26.0 (26.1)	23.6 (23.7)	1.5 (1.5)	4.2 (4.3)
$VO(SO_3CF_3)_2.2Py$	9.6 (9.7)	12.2 (12.2)	21.6 (21.8)	27.2 (27.5)	1.8 (1.9)	5.2 (5.3)
$VO(SO_3CF_3)_3.2Py$	7.4 (7.6)	14.4 (14.3)	25.1 (25.4)	23.4 (23.2)	1.4 (1.5)	4.1 (4.2)
$V(SO_3CF_3)_3.2TPPO$	4.7 (4.8)	9.0 (9.1)	16.0 (16.2)	44.0 (44.4)	2.6 (2.8)	-
$VO(SO_3CF_3)_2.2TPPO$	5.3 (5.5)	6.7 (6.9)	12.0 (12.4)	48.9 (49.5)	3.1 (3.2)	-
$VO(SO_3CF_3)_3.2TPPO$	4.7 (4.8)	9.1 (9.0)	15.7 (16.0)	42.9 (43.7)	2.6 (2.8)	-
$V(SO_3CF_3)_3.bipy$	7.7 (7.8)	14.6 (14.7)	26.2 (26.1)	23.4 (23.8)	1.2 (1.2)	4.1 (4.3)
$VO(SO_3CF_3)_2.bipy$	9.6 (9.8)	12.0 (12.3)	21.8 (21.9)	27.6 (27.6)	1.4 (1.5)	5.2 (5.4)
$VO(SO_3CF_3)_3.bipy$	7.3 (7.6)	14.1 (14.3)	25.0 (25.5)	22.6 (23.3)	1.1 (1.2)	4.1 (4.2)

$$V(O_2CCF_3)_3 + 3CF_3SO_3H \quad V(SO_3CF_3)_3 + 3CF_3COOH \quad (1)$$

$$VO(O_2CCF_3)_2 + 2CF_3SO_3H \quad VO(SO_3CF_3)_2 + 2CF_3COOH \quad (2)$$

$$VOCl_3 + 3CF_3SO_3H \quad VO(SO_3CF_3)_3 + 3HCl \quad (3)$$

Also the reaction of VCl_3 and $VOCl_2$ with CF_3SO_3H at reflux temperature resulted in the formation of $V(SO_3CF_3)_3$ and $VO(SO_3CF_3)_2$ respectively. The easy replacement of a CF_3CO_2 group by CF_3SO_3 [14] and SO_3F [15-17] has been noted in similar reactions.

Compounds

A (green), B (sky blue) and C (dark green) are fine solid powders insoluble in common organic (non-coordinating) solvents as well as in trifluoromethanesulfonic acid. A-C are thermally stable *in vacuo* up to 160, 200 and 170°C respectively. The lack of solubility of compounds in trifluoromethanesulfonic acid and their inability to volatilize even at elevated temperature may be due to their polymeric nature.

Thermal analysis

Thermograms of A-C recorded up to 600°C in the presence of air reveal that these trifluoromethanesulfonates are stable up to 120°C at ambient pressure (more stable *in vacuo*). The weight losses (120-420°C) observed for A-C are 81.6, 75.9 and 81.8% respectively. These agree well with the theoretical values (81.7, 75.1 and 82.3%) for the formation of V_2O_5 in each case. The latter was characterized as the sole product of decomposition. No further loss in weight was observed after 420°C. The volatiles were not characterized.

Infrared spectra

The i.r. spectra of A-C have been examined in the range 2000-400 cm^{-1}. The three S-O stretching modes (A: 1325s,b, 1135s, 1034s,b; B: 1320s,b, 1130vs, 1054s; C: 1300s,b, 1153m,

1034s) suggest a bridging bidentate nature for the SO_3CF_3 group (C_{3v} symmetry). These bands are in good agreement with the corresponding bands in $Me_3SnSO_3CF_3$ [18] and $Me_2Sn(SO_3CF_3)_2$ [19], where bridging bidentate SO_3CF_3 groups have been proposed on the basis of vibrational and ^{119}Sn Mössbauer studies and a structural study on the analogous compound $Me_2Sn(SO_3F)_2$ [20]. The intense bands at 1024 and 1005 cm^{-1} in B and C respectively are attributed [21] to the discete V=O group, ruling out any possibility of polymerization through the V=O. The bands around 1200 cm^{-1} (A: 1215-1245s,b, 1160m; B: 1228m,b, 1208sh, 1185m; C: 1205-1240, 1199s) may be attributed to CF_3. Weak to medium intensity bands in A, B and C at 775, 770 and 770cm^{-1}, respectively, may be due to S-C,. The CF_3 (A: 640s, 518s; B: 640s, 520s; C: 640s, 520s cm^{-1}) and SO_3 (A: 575w, B: 585w, C: 570m cm^{-1}) deformation modes agree with the corresponding modes in $Me_3SnSO_3CF_3$.

Bands in $I(SO_3CF_3)_3$ at 1420, 1210 and 830 cm^{-1} have been attributed to S-O of monodentate, while at 1320, 1120 and 980 cm^{-1} to bidentate SO_3CF_3 groups [22]. The magnitudes of S-O in the complexes (A: 2Py: 1430, 1310, 1210, 1130, 970, 840; B.2Py: 1430, 1315, 1210, 1145, 985, 840; A.bipy: 1400, 1320, 1235, 1140, 965, 840; B.bipy: 1400, 1310, 1250, 1130, 995, 840; A.2TPPO: 1420, 1325, 1210, 1140, 985, 845; B.2TPPO: 1420, 1330, 1210, 1120, 992, 845 cm^{-1}) of A and B with pyridine, 2,2'-bipyridyl and triphenylphosphine oxide suggest both mono- as well as bi-dentate SI_3CF_3 groups in them. The bands around 1435, 1205, and 855 cm^{-1} in C.2Py, C.bipy and C.2TPPO suggest only monodentate SO_3CF_3 groups in them. The V=O in all these complexes appear between 970-990 cm^{-1}; substantially at a

lower value than in the parent trifluoromethanesulfonate. This may be due to the change in V=O bond order as a result of the increased electron density at vanadium. Expected shifts in the ligand vibrations [23-25] have been observed in the complexes.

Diffuse reflectance spectra

Absorption bands at 14.9 and 21.7 kK in A appear to be from transitions $^3T_{1g}(F)$ $^3T_{2g}(F)$ and $^3T_{1g}(F)$ $^3T_{1g}(P)$, respectively [26,27]. These values are in close accord with similar values [4,27] where six-coordination around vanadium has been proposed.

The diffuse reflectance spectrum of B reveals three bands at 12.5, 15.0 and 23.5 kK from the transitions $^2B_2$ ^2E, $^2B_2$ $^2B_1$ and $^2B_2$ $^2A_1$, respectively [26]. The weak bands above 30 kK [28] may be attributed to charge-transfer bands. The pattern of electronic spectrum in B compares well with either five or six coordinated oxovanadium (IV) systems [29,30] It is thus not possible to allocate unambiguously a particular coordination number to vanadium in this compound.

Magnetic properties

A and B have magnetic moment values of 2.7 and 1.65 B.M. at 298 K, respectively. Values slightly below the spin-only value are a common feature of V(III) and V(IV) compounds, either due to spin orbit coupling or their polymeric nature. As expected C is found to be diamagnetic.

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