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Preparation of some Fluoroalkoxy Oxovanadium(V) Derivatives and their Insertion Reactions with Phenyl Isocyanate

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New derivatives of oxovanadium(V) containing the fluoroalkoxy ligand $OR_f = OCH_2CF_3$ *have been prepared by reacting* $VO(Oi\text{-}Pr)_{3-x}Cl_x$ *on* $LiOR_f$. ^1H *and* ^{19}F *NMR and infrared spectra were recorded. From the chemical shifts of the isopropyl group and* $\nu_{(V=O)}$ *stretching frequencies, the electron donating character of the* OCH_2CF_3 *group is found in the intermediate position:* $Cl < OCH_2CF_3 < Oi\text{-}Pr$.

The insertion reaction of phenyl isocyanate PhNCO in the vanadium–oxygen bond gives new urethanes, which have been characterized by spectroscopy and hydrolysis products. Insertion takes place in the vanadium trifluoroalkoxy bond less readily than in the vanadium alkoxy bond.

Introduction

As part of a programme on the synthesis and reactivity of organic compounds of vanadium(V), we found it interesting to investigate fluoroalkoxides. The behaviour of such derivatives is expected to be appreciably different from usual alkoxides since the inductive effect of the fluorine atoms of fluoroalkoxy groups such as OCH_2CF_3, $OCH(CF_3)_2$ *etc.*, previously reported in aluminium, titanium *etc.* chemistry, was found to increase definitely the sensitivity of the central metal atom to nucleophilic attack [1–4].

Very little work has been so far reported concerning fluoroalkoxy compounds of vanadium(V). Previous experiments have shown that the treatment of $VOCl_3$ with the alcohol 2,2,3,3-tetrafluoropropanol ($R_f'OH = CF_2HCF_2CH_2OH$) gave both $VO(OR_f')_3$ and $VOCl(OR_f')_2$ [5].

We now describe the preparation and characterization of some mixed compounds $VO(Oi\text{-}Pr)_{3-x}(OR_f)_x$ (x = 1–3) and $VOCl(OR_f)_2$ with OR_f = 2,2,2-trifluoroethoxy group OCH_2CF_3. Their reactivity towards acetyl chloride and phenyl isocyanate is also reported.

Results and Discussion

Attempts to synthesize $VO(OR_f)_3$ by action of R_fOH on $VO(Oi\text{-}Pr)_3$ were unsuccessful, in contrast with similar experiments in titanium chemistry [2, 3]. However, by reacting the organolithium compound $LiOR_f$ with the appropriate chloroalkoxide $VO(Oi\text{-}Pr)_{3-x}Cl_x$, the following reaction occurred:

$$VO(Oi\text{-}Pr)_{3-x}Cl_x + xLiOR_f \longrightarrow VO(Oi\text{-}Pr)_{3-x}(OR_f)_x + xLiCl\ (x = 1, 2, 3)$$

$$VOCl_3 + 2LiOR_f \longrightarrow VOCl(OR_f)_2 + 2LiCl$$

These very hygroscopic compounds are purified by distillation as yellow-orange liquids. The volatile $VOCl(OR_f)_2$ can also be obtained by redistribution between $2VOCl_3$ and $VO(OR_f)_3$. Attempts to isolate the dichlorotrifluoroethoxy complex $VOCl_2(OR_f)$ from the reaction between $VOCl_3$ and $LiOR_f$ or $VOCl_3$ and $2VO(OR_f)_3$ failed, the final product being always contaminated with $VOCl_3$.

All of these fluoroalkoxy derivatives are monomeric in benzene solution and non ionic. Their ^1H and ^{19}F NMR data and $\nu_{(V=O)}$ infrared frequencies are listed in Table I.

The following sequence of electron donating ability for the anionic ligand

$$Cl < OR_f < Oi\text{-}Pr$$

may be deduced, consistent with previous works on other series [6, 7]. Compared to the usual alkoxides of vanadium, the trifluoroalkoxy $VO(OR_f)_3$ should be more sensitive to nucleophilic reagents.

Substitution reaction occurred by reaction of $VO(OR_f)_2(Oi\text{-}Pr)$ with acetyl chloride to give $VO(OR_f)(Oi\text{-}Pr)Cl$, in agreement with the fact that the fluoroalkoxy group OCH_2CF_3 is a better leaving group than the alkoxy one Oi-Pr.

Insertion of PhNCO in various metal alkoxide compounds, according to the reaction:

$$M\text{–}OR + PhNCO \longrightarrow M\text{–}N(Ph)COOR$$

is well known [8–10]. The formation of the urethane complex may be followed by the complete disappearance of the isocyanate infrared absorption at 2250 cm^{-1} and the appearance of the C=O stretching band near 1700 cm^{-1}. However, such reactions are

TABLE I. ^1H and ^{19}F NMR Data and $\nu_{(V=O)}$ Stretching Frequency.

Compound	$^1H^a$				$^{19}F^b$	
	$OC\mathit{H}(CH_3)_2$	$OCH(C\mathit{H}_3)_2$	$OC\mathit{H}_2CF_3$	J_{H-F}	$OCH_2C\mathit{F}_3$	$\nu_{(V=O)}$ cm^{-1}
$VO(Oi\text{-}Pr)_3$	5.30	1.43				1005
$VO(Oi\text{-}Pr)_2(OR_f)$	5.40	1.46	5.06	8.8	+2.0	1010
$VO(Oi\text{-}Pr)(OR_f)_2$	5.42	1.50	5.21	8.5	+1.8	1015
$VO(OR_f)_3$			5.48	8.0	+1.2	1025
$VOCl(OR_f)_2$			5.65	7.5	+2.3	1030
$CF_3CH_2OH^c$			3.93	7.0	−1.0	

[a] Chemical shifts in ppm downfield with respect to TMS for ^1H, in CCl_4 solvent. [b] Chemical shifts in ppm downfield with respect to CF_3CO_2H for ^{19}F in CCl_4 solvent; J_{H-F} coupling constant in Hz. [c] Measured as neat liquid.

unknown in vanadium alkoxide chemistry, whereas $VOCl_3$ was reported to give an addition compound $VOCl_3 \cdot 2PhNCO$ [13]. We investigated insertion reactions in the vanadium oxygen bond in VOi-Pr and VOR_f bond respectively.

In the case of isopropoxy vanadate $VO(Oi\text{-}Pr)_3$ mono (and tri) insertion reactions were observed at room temperature when 1 (or 3) equivalents of PhNCO were added. $VO(Oi\text{-}Pr)_2(N(Ph)COOi\text{-}Pr)$ and $VO(N(Ph)COOi\text{-}Pr)_3$ were isolated as red liquids with $\nu_{(C=O)}$ at 1725 cm^{-1}. Hydrolysis of these complexes gives the urethane HN(Ph)COOi-Pr in quantitative yields. In the case of trifluoroethoxy vanadate $VO(OR_f)_3$ similar insertions occur with $VO(OR_f)_3$, under refluxing conditions, to give the red liquid $VO(OR_f)_2(N(Ph)COOR_f)$ and brown solid $VO(N(Ph)COOR_f)_3$ with $\nu_{(C=O)}$ at 1735 cm^{-1}. Hydrolysis gives the fluoroalkoxy urethane $HN(Ph)COOR_f$ in quantitative yields.

In the case of the mixed $VO(Oi\text{-}Pr)_2(OR_f)$ the mono insertion product, (with 1 equivalent of PhNCO), shows an infrared spectrum with $\nu_{(C=O)}$ at 1740 cm^{-1}. HN(Ph)COOi-Pr was found after hydrolysis which is indicative of the insertion of phenyl isocyanate occurring preferably in the VOi-Pr bond rather than in the VOR_f bond.

^1H NMR spectra show characteristic but complex signals of both the urethane and isopropoxide (or fluoroethoxide) protons. The presence of an equilibrium in solution with the starting isocyanate and the alkoxide – as already reported by Meth-Cohn [8] in the case of $Ti(OR)_n$ + $_nRNCO$ – is suggested. Also non-equivalence due to the bulky urethano group around the central atom must be considered to explain the complexity of the spectra, for example the three doublets of the methyl protons in $VO(N(Ph)COOi\text{-}Pr)_3$.

Experimental

Starting Materials

The lithium reagent $LiOR_f$ was obtained as a white precipitate by action of 2,2,2-trifluoroethanol R_fOH = CF_3CH_2OH on LiBu in pentane at −60 °C to avoid vigorous reaction. Mixed $VO(Oi\text{-}Pr)_{3-x}Cl_x$ (x = 0, 3) were prepared by a method mentioned in literature [11, 12]. All solvents (pentane, benzene, toluene) were dried by means of sodium wire or molecular sieves. Rigorous precautions were taken to exclude moisture in experiments and manipulations were carried out in a nitrogen atmosphere.

Physical Measurements

Infrared data were obtained using a Perkin-Elmer Model 557 spectrophotometer and KBr plates. ^1H and ^{19}F NMR spectra were respectively recorded on Perkin Elmer R12 and R10 spectrometers, using CCl_4 solutions with TMS as internal standard and CF_3COOH as external standard.

Molecular weight determinations were made cryoscopically in benzene. Conductivity measurements were obtained from benzene solutions with a Philips PW 950 conductivity bridge.

Elemental Analysis

C, H were performed by the Service Central de Microanalyse du CNRS; vanadium was determined as ignited V_2O_5, after hydrolysis of the sample. The analytical data are listed in Table II.

TABLE II. Analytical Data.

Compound	%C exp (calc)	%H exp (calc)	%V exp (calc)
$VO(Oi\text{-}Pr)_2(OR_f)$	34.0 (33.8)	5.8 (5.6)	18.0 (18.0)
$VO(Oi\text{-}Pr)(OR_f)_2$	26.9 (25.9)	3.7 (3.4)	15.2 (15.7)
$VO(OR_f)_3$	19.4 (19.8)	1.8 (1.6)	14.4 (14.0)
$VOCl(OR_f)_2$	17.0 (16.0)	1.9 (1.3)	17.1 (17.0)
$VOCl(Oi\text{-}Pr)(OR_f)$	23.0 (23.0)	3.5 (3.5)	19.8 (19.6)

TABLE III. Preparation of the Complexes.

Compound	Physical Aspect	Starting Material (mmol)	$LiOR_f$ (mmol)	B.P. °C/mmHg	% Yield
$VO(Oi\text{-}Pr)_2(OR_f)$	Yellow liquid	$VOCl(Oi\text{-}Pr)_2$ (13.6)	(13.6)	40/0.01	70
$VO(Oi\text{-}Pr)(OR_f)_2$	Yellow liquid	$VOCl_2(Oi\text{-}Pr)$ (35.5)	(71)	52/0.5	70
$VO(OR_f)_3$	Yellow liquid	$VOCl_3$ (17.8)	(53.4)	55/0.1	60
$VOCl(OR_f)_2$	Orange liquid	$VOCl_3$ (77.3)	(154.6)	105/100	60

Preparation of the Complexes

Since the method is a general one, only one example is given. Details for all complexes prepared are collected in Table III.

Preparation of $VO(Oi\text{-}Pr)_2(OR_f)$

To a suspension of $LiOR_f$ in 20 ml pentane (13.6 mmol) was added $VO(Oi\text{-}Pr)_2Cl$ (13.6 mmol) in 10 ml pentane, at −20 °C, with a constant stirring. Then the mixture was allowed to warm to room temperature, refluxed 1/2 hr and filtered to eliminate LiCl. After removal of the solvent, the residue was distilled under vacuum.

Reaction of Acetyl Chloride

To $VO(Oi\text{-}Pr)_2(OR_f)$ (1.38 g, 4.26 mmol) in 5 ml pentane was added acetyl chloride (0.33 g, 4.26 mmol) in 5 ml pentane, at −20 °C, with a continuous stirring. After addition, the mixture was allowed to warm to room temperature, the solvent removed under vacuum and trapped at −78 °C. 2,2,2-trifluoroacetate, $CF_3CH_2COOCH_3$, was checked by ^1H NMR. Distillation of the residue gave a clear yellow liquid, $VOCl(Oi\text{-}Pr)(OR_f)$ (b.p.: 36 °C/0.01 mm). Yield: 50%. ^1H NMR data: i-Pr doublet, 1.58 ppm: unresolved septet overlapped by the OR_f signals, OR_f quartet, 5.39 ppm. IR: $\nu_{(V=O)} = 1020\ cm^{-1}$.

Insertion Reactions with Phenyl Isocyanate

As a general method, the alkoxide was treated with the required molar amount (1 or 3 equivalents) of PhNCO in the same solvent (for $VO(Oi\text{-}Pr)_3$ in pentane or benzene at 0 °C; for $VO(OR_f)_3$ in benzene or toluene) with 5 hr refluxing. After removing the solvent, the residue was dried several hours, under reduced pressure, to yield the final product. Attempts to distill the product were unsuccessful, owing to ready decomposition. ^1H NMR data. $VO(N(Ph)COOi\text{-}Pr)_3$: septet, 5.08 ppm; doublet, 1.32 ppm. $VO(N(Ph)COOR_f)_3$: quartet, 5.26 ppm.

Hydrolysis of the Urethane Compounds

Very generally, to a weighed amount of the insertion product in 10 ml pentane, water was added in slight excess (1.2 or 3.2 equivalent respectively). Contents were shaken and V_2O_5 filtered out. HN(Ph)-COOi-Pr and $HN(Ph)COOR_f$ could be recrystallized from benzene, weighted and identified by ^1H NMR, IR data and melting point. HN(Ph)COOi-Pr. ^1H NMR: septet 4.93, doublet 1.23 ppm. IR: $\nu_{(NH)}$, 3300 cm^{-1}, $\nu_{(C=O)}$, 1690 cm^{-1}. M.p. 87 °C. HN(Ph)-$COOR_f$. ^1H NMR: quartet 4.51 ppm. IR: $\nu_{(NH)}$, 3100 cm^{-1}, $\nu_{(C=O)}$, 1715 cm^{-1}. M.p. 70 °C.

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