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The Reaction of tris(Methanol) Vanadium(IV)-oxidedichloride with Nitrogen Donors

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The reactions of $VOCl_2,3CH_3OH$ with a range of aliphatic and heterocyclic nitrogen donor ligands have been studied, and it has been shown that the pK_a, bulk of the ligand, and the reaction conditions all influence the stoichiometry of the product. Complexes with various monodentate (L and L′) and bidentate chelating (B) and bridging (B′) ligands have been isolated with stoichiometries: $VOCl_2,xL$ (x = 2 and 3), $VoCl_2.xL,yCH_3OH$ (x = 1, 2; y = 1, 2), $VOCl_2,B$, $2VOCl_2,3B'$, $(LH)(VOCl_2(OCH_3))$, $(BH_2)(VOCl_2(OCH_3))_2$, $(B'H)(VOCl_2(OCH_3))$, $VO(OCH_3)_2$, 2LHCl, $VO(OCH_3)_2,BH_2Cl_2$, $VOCl(OCH_3),xL$ (x = E and 2), and $VOCl(OCH_3),2L,L'HCl$. The complexes have been characterised by measurements of infrared and electronic spectra, conductivity and magnetic measurements.

Introduction

The vanadium(IV) alkoxides have received little attention. $VCl_2(OCH_3)_2CH_3OH$ was reported[1] to be the product of the reaction between vanadium(IV) chloride and methanol, but subsequently it was shown to be $VOCl_2,3CH_3OH$.[2] As it is well kown[3] that the addition of nitrogen bases facilitates the alcoholysis of transition metal halides, the reactions of $VOCl_2$, $3CH_3OH$ with such bases seemed worthy of study. The bases were chosen to give a range of pK_a values and ligand bulk.

Discussion

The analytical data of the various reaction products are summarised in Table I. It can be seen that product stoichiometry depends on reaction conditions. Broadly speaking, an excess of $VOCl_2$, $3CH_3OH$ produces salts of the anion $[VOCl_2(OCH_3)]^-$, but an excess of ligand gives simple complexes of $VOCl_2$ with the ligand although complexes of $VOCl(OCH_3)$ may be isolated in one or two instances. The reactions are conveniently discussed according to the three sets of preparative conditions (see experimental). These are (1) reaction in diethylether with V: Ligand = 5:4, (2) reaction in diethylether with V: Ligand = 1:4, and (3) reaction with excess of neat ligand.

(1) *Reactions with an excess of $VOCl_2,3CH_3OH$.* With two exceptions (2,2′-bipyridyl and 2,6-dimethylpyrazine), all ligands react under these conditions to give the protonated base and the anion $[VOCl_2(OCH_3)]^-$. Monobasic ligands give the 1:1 species $(LH)[VOCl_2(OCH_3)]$, where L = pyridine, 2-methyl pyridine, 3-methyl pyridine, 4-methyl pyridine, 2,6-dimethyl pyridine, 3,5-dimethyl pyridine, quinoline, *iso-quinoline,* diethylamine, triethylamine, N,N-dimethylbenzylamine N,N-dimethylaniline. The bidentate ligand 4,4′-bipyridyl gives both a 1:1 and 1:2′ complex, containing respectively the mono- and di-protonated ligand, but N,N,N,′N′-tetramethyl-1,2-diaminoethane gives only the 1:2 complex. Conductance values for $\sim 10^{-3}$ *M* solutions in methanol (see experimental) correspond to the formulation as ionic 1:1 and 1:2 complexes, and although plots of Λ_m against $\sqrt{c}$ are not linear, this is not unexpected in view of probable ion-pairing and hydrogen bonding.

The infrared spectra of these complexes confirm the presence of protonated rather than co-ordinated ligands, with N-H stretching frequencies in the range 2700-3400 cm^{-1}. This appreciable shift from the values (2000-2700 cm^{-1}) found for the amine hydrochlorides, which is attributed[4,5,6] to a change in the degree of hydrogen bonding when the halide ion is replaced by a larger anion, shows that the products are not mixtures containing amine hydrochloride.

Also extraction of the complexes with solvents in which the hydrochlorides are soluble did not alter the analyses. νC-O(*ca.* 1020 cm^{-1}), νV=O(*ca.* 990 cm^{-1}), νV-OC (*ca.* 585 cm^{-1}) characterised the anion, and two strong bands around 455 and 355 cm^{-1} may be assigned to V-Cl stretching modes. c.f. VCl_4 475 cm^{-1} and VCl_4^- 406 cm^{-1}.[7,8,9] The relative simplicity of the νV-Cl stretching region suggests that the anion is four-co-ordinate, since polymeric species would show more complex spectra.

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Table I. Analytical Data.

Ligand	pK_a[a]	Complex	Colour			Found					Calculated			Method of Preparation
				%C	%H	%N	%Cl	%V	%C	%H	%N	%Cl	%V	
Pyridine	5.23	(pyH)(VOCl$_2$OMe)	turquoise-blue	28.9	3.5	5.6	28.6	20.4	28.9	3.6	5.6	28.5	20.4	1 (see experimental section)
		VOCl$_2$,2py	light turquoise-blue				24.0	17.4				24.0	17.4	3
		VOCl$_2$,3py	bright turquoise-blue				18.9	13.6				18.9	13.6	3
2-methyl-pyridine	6.48	(2-mpyH)(VOCl$_2$OMe)	turquoise-blue				26.8	19.0				27.0	19.4	1
		VOClOMe,2mpy	bright blue	36.5	4.5	6.8	15.3	21.8	37.1	4.5	6.2	15.0	21.5	3
3-methyl-pyridine	6.00	(3-mpyH)(VOCl$_2$OMe)	turquoise-blue	31.9	3.9	5.3	26.4	19.4	31.9	3.8	5.3	27.0	19.4	1
		VOCl$_2$,2(3-mpy)	light turquoise-blue				22.2	15.7				21.9	15.7	3
		VOCl$_2$,3(3-mpy)	bright turquoise-blue				17.0	12.4				17.0	12.2	2
		VOClOMe,2(3-mpy)	apple green	51.9	5.4	9.1	11.5	15.9	51.4	5.6	9.2	11.2	16.0	3
4-methyl pyridine	6.00	(4-mpyH)(VOCl$_2$OMe)	turquoise-blue	31.5	4.0	5.2	26.7	19.3	31.9	3.8	5.3	27.0	19.4	1
		VOCl$_2$,2(4-mpyH)	turquoise-blue	43.7	4.3	8.3	21.6	15.8	44.5	4.3	8.6	21.9	15.7	3
		VOCl$_2$,3(4-mpy)	turquoise-blue	52.0	5.0	10.0	16.7	12.1	51.8	5.1	10.1	17.0	12.2	2 or 3
2,6-dimethyl pyridine	6.30[b]	(2,6-dmpyH)(VOCl$_2$OMe)	turquoise-blue	34.4	4.7	5.0	25.3	18.1	34.7	4.7	5.1	25.6	18.4	1
		VO(OMe)$_2$,2(2,6-dmpyH)	grey-green	46.7	6.7	6.8	17.1	12.1	46.2	5.8	6.7	17.0	12.2	3
3,5-dimethyl pyridine	6.31	(3,5-dmpyH)(VOCl$_2$OMe)	turquoise-blue	34.1	4.8	4.8	25.4	18.3	34.7	4.7	5.1	25.6	18.4	1
		VOCl$_2$,2(3,5-dmpy)	turquoise-blue	47.6	5.4	7.9	19.8	14.3	47.8	5.2	8.0	20.1	14.5	2
		VOClOMe,3,5-dmpHCl	green				14.6	10.1				14.4	10.4	3
Quinoline	4.80	(quinH)(VOCl$_2$OMe)	light green				23.3	17.1				23.7	17.0	1
		(quinH)(VOCl$_2$OMe, quin)	light green	53.6	4.4	6.6	17.0	11.8	53.3	4.0	6.5	16.9	11.9	2 or 3
i-Quinoline	5.14	(i-quinH)(VOCl$_2$OMe)	light turquoise blue	40.1	3.4	4.7	23.6	17.1	40.0	3.3	4.7	23.7	17.0	1
		VOCl$_2$,2i-quin	bright green	54.9	3.9	6.9	17.5	13.1	54.6	3.5	7.1	17.9	12.9	3
		VOCl$_2$,3i-quin	light green	62.8	4.1	8.1	11.7	8.5	61.7	4.0	8.0	11.3	8.2	3
4,4'-Bi-pyridyl	4.81	(4,4'-bipyH)(VOCl$_2$OMe)	dark yellow-green				22.2	15.6				21.8	15.6	1
		(4,4'-bipyH$_2$)(VOCl$_2$OMe)$_2$	dark yellow-green				28.5	20.1				28.6	20.5	1
		2VOCl$_2$,3(4,4'-bipy)	yellow				19.6	13.7				19.1	13.7	2
2,2'-Bi-pyridyl	4.51	VOCl$_2$,2,2'-bipy	yellow-green				23.7	17.0				24.1	17.3	1
2,6-Dimethyl-pyrazine	1.50[c]	VOCl$_2$,dmp,2MeOH	light green				22.8	16.3				22.8	16.4	1
		VOCl$_2$,dmp,MeOH	brown				25.3	18.4				25.5	18.3	3
		VOCl$_2$,2dmp,MeOH	blue	40.4	5.2	14.8	18.3	13.4	40.4	4.9	14.5	18.4	13.2	2
Diethylamine	10.98	(Et$_2$NH$_2$)(VOCl$_2$OMe)	turquoise-blue				28.6	20.7				29.2	21.0	1
		VO(OMe)$_2$,2Et$_2$,NH$_2$Cl	grey-green				19.5	13.7				20.4	14.6	2 or 3
		VOClOMe,2py,Et$_2$NH$_2$Cl	light green				17.9	12.9				17.7	12.7	4
Triethylamine	10.76	(Et$_3$NH)(VOCl$_2$OMe)	turquoise-blue				25.9	19.1				26.2	18.8	1
		VO(OMe)$_2$,2Et$_3$NHCl	grey-green				17.3	12.4				17.5	12.6	2 or 3
		VOClOMe,2py,Et$_3$NHCl	light green				16.3	11.7				16.5	11.9	4
N,N-Dimethyl benzylamine	9.37	(BzNMe$_2$H)(VOCl$_2$OMe)	turquoise-blue	39.0	5.4	4.5	23.0	16.4	39.4	5.2	4.6	23.3	16.7	1
		VO(OMe)$_2$,2BzNMe$_2$HCl)	grey-green				15.3	10.9				15.6	10.9	3
N,N-Dimethyl aniline	5.06	(PhNMe$_2$H)(VOCl$_2$OMe)	turquoise-blue	34.9	5.2	4.6	24.5	17.2	34.0	5.2	4.8	24.4	17.5	1, 2 or 3
N,N,N'-N'-tetra methyl-1,2-diaminoethane	10.17	(trenH$_2$)(VOCl$_2$OMe)$_2$	turquoise-blue	20.2	5.3	6.1	30.8	22.2	21.1	4.8	6.1	31.1	22.3	1
		VO(OMe)$_2$,trenH$_2$Cl$_2$	grey-green				22.2	16-2				22.3	16.0	2 or 3

[a] pK_a values taken from Chemical Society Special publication Number 17, 1964, 'Stability Constants'. [b] Estimated value, position of substituents has very little effect on pK_a. [c] Value for pyrazine, substituents may increase value slightly.

2,2'-bipyridyl does not yield a salt but instead gives a simple complex VOCl$_2$,bipy, presumably because of the great tendency of the ligand to form chelates. 2,6-Dimethylpyrazine (dmp), which has a low pK_a value, forms VOCl$_2$,2CH$_3$OH,dmp, which on heating loses a molecule of methanol. The infrared spectra of both dmp complexes show a νOH band at 3,300 cm^{-1} and bands typical of the co-ordinated monodentate pyrazine,[10] but no bands that can be attributed to a V-OCH$_3$ group or the protonated base.

(2) *Reactions in diethylether with* 1:4 *VOCl$_2$, 3CH$_3$OH: ligand ratio.* Two types of complexes could be isolated, simple adducts of VOCl$_2$, and products that are best considered mixtures of VO(OCH$_3$)$_2$ and the aminehydrochloride. Pyridine, 3-methyl pyridine, 3,5-dimethyl pyridine and isoquinoline give products whose analyses are between VOCl$_2$, 2L and VOCl$_2$, 3L but which on warming in vacuo or shaking with diethylether give VOCl$_2$,2L. With 3-methyl pyridine (L) the adduct VOCl$_2$,3L is formed. The infrared spectra of these compounds show bands characteristic of the co-ordinated ligands but no bands that could be attributed to the protonated base or a V-OCH$_3$ grouping. 4,4'-bipyridyl gives a complex of stoichiometry 2VOCl$_2$, 3(4,4'-bipy), the infrared spectrum of which indicates that both nitrogen atoms of the ligand are co-ordinated; this suggests a polymeric structure. 2,2'-bipyridyl gives no characterisable product.

Diethylamine and triethylamine give products of stoichiometry VO(OCH$_3$)$_2$, 2LHCl, and N,N,N',N'-tetramethyl-1,2-diaminoethane gives the analogous product VO(OCH$_3$)$_2$, trenH$_2$Cl$_2$. These complexes are mixtures of VO(OCH$_3$)$_2$ and the amine hydrochloride since there is no infrared evidence for the [VO(OCH$_3$)$_2$Cl$_2$]$^{2-}$ anion.

N,N-dimethylaniline gives the complex (C$_6$H$_5$NH(CH$_3$)$_2$) (VOCl$_2$(OCH$_3$)), and quinoline forms (quinH) (VOCl$_2$(OCH$_3$),quin); the infrared spectra of the products correspond to the formulations given. It is interesting to note that even with reactions involving neat ligand (see next section) no further methanolysis results, presumably because of the relatively low pK_a of the bases.

(3) *Reactions of VOCl$_2$, 3CH$_3$OH with neat ligand.* 1:3 Complexes result from reactions with pyridine, 4-methylpyridine, and iso-quinoline, the analytical data and infrared spectra showing that no methanolysis takes place. With 2-methylpyridine and 3-methylpyridine partial methanolysis takes place and VOCl(OCH$_3$), 2-mpy and VOCl(OCH$_3$), 2(3-mpy) are formed respectively; the infrared spectra of the complexes confirm the presence of the co-ordinate methyl pyridine and a methoxy group. 3,5-dimethylpyridine appears to form an analogous complex, but as 3,5-dimethylpyridine hydrochloride is insoluble in 3,5-dimethylpyridine(L) the product has the stoichiometry VOCl(OCH$_3$)L,LHCl. In contrast 2,6-dimethylpyridine(L) forms VO(OMe)$_2$,2LHCl.

Spectra and magnetic susceptibility. Species containing VOCl$_2$ groupings show two V-Cl stretching modes, but only one is found in compounds containing the VOCl(OCH$_3$) moiety. The V-OCH$_3$ modes are

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[10] A.P.B. Lever, J. Lewis and R.S. Nyholm, *J. Chem. Soc.*, 1963, 5042.

very sensitive to the co-ordination number of vanadium, compounds with the highest co-ordination number showing the absorbance at lowest frequency (e.g. VOClOMe,2-mpy 584 cm^{-1} and VOClOMe,2(3-mpy) 508 cm^{-1}). All complexes show electronic spectra typical of the V^{IV} $V=O$ grouping [11] and magnetic moments close to the spin only value (*ca.* 1.72 BM).

Conclusions

The reactions indicate that methanolysis is favoured by bulky ligands with a high pK_a. Thus with an excess of $VOCl_2$, $3CH_3OH$ partial methanolysis takes place with the majority of bases. With increasing ligand concentration, adducts form with ligands of high pK_a provided there is no steric problem, but sterically-hindered ligands generally promote complete methanolysis and the formation of $VO(OCH_3)_2$. When the complexes $(LH)[VOCl_2(OCH_3)]$, where L is 2,6-dimethylpyridine or N,N-dimethylaniline (bulky ligands with relatively low pK_a values), are allowed to react with pyridine, a simple pyridine adduct ($VOCl_2$, 2py) forms and the free base and methanol are liberated. In contrast, the analogous reactions involving complexes where the base has a high pK_a (e.g. triethylamine and diethylamine), give compounds $VOCl(OCH_3)$,2py,LHCl. No reaction occurs when $[(C_2H_5)_3NH][VOCl_2(OCH_3)]$ is treated with a bulky ligand of low pK_a such as 2,6-dimethylpyridine.

Experimental Section

Analysis. Carbon, hydrogen, and nitrogen analyses were carried out in the Department by means of an F and M Anlayser, but in many cases they were not reproducible because of the ease with which the compounds were hydrolysed. Vanadium was determined by ignition of a wheighed sample to V_2O_5 at 550°C. For chloride determination (gravimetrically as AgCl) the sample was first hydrolysed in dilute nitric acid.

Measurement of spectra and magnetic properties. Infrared spectra (200-4,000 cm^{-1}) were measured as nujol and H.C.B. mulls by means of Perkin Elmer 457 and Grubb-Parson DM4 spectrometers. Electronic reflectance spectra (5,000-50,000 cm^{-1}) were recorded by means of a Unicam SP 700C spectrometer fitted with a diffuse reflectance attachment, MgO being used as reference. Magnetic susceptibilities were determined at room temperature by the Gouy method.

Conductivities. Conductivities were measured on solutions in methanol at 25°C by means of a Pye 11700 conductance bridge over a 10 fold concentration range. Selected values of Λ_m quoted in ohm^{-1} cm^2 mole^{-1} with the appropriate concentration in mole $l^{-1} \times 10^3$ in brackets: pyHCl 112(1.22); (pyH)$(VOCl_2OMe)$ 149 (1.48); $(trenH_2)(VOCl_2OMe)_2$ 260 (1.10); (4,4'-bipyH)$(VOCl_2OMe)$ 155 (1.30); (4,4'-bipy$H_2)(VOCl_2OMe)_2$ 236 (1.18).

Starting materials. The ligands, which were commercially available materials, were dried over phosphoris oxide or calcium hydride before use. Diethylether was dried initially over sodium wire and then distilled from a potassium mirror. Methanol was dried with 3A molecular sieves. $VOCl_2,3CH_3OH$ was prepared by the direct reaction in carbon tetrachloride of VCl_4 and CH_3OH.[2] Found: Cl, 30.2; V, 21.8. $VOCl_2,3CH_3OH$ requires: Cl, 30.3; V, 21.8%.

Reaction of $VOCl_2,3CH_3OH$ with nitrogen ligands. All manipulations were performed in an all-glass vacuum line or a nitrogen-filled dry box. The complexes (c.f. Table I) were prepared by one of the following procedures:

1. A solution of the ligand ,0.008 mol monodentate and 0.004 mol bidentate) in diethylether was added to a solution of $VOCl_2,3CH_3OH$ (0.01 mol) in diethylether (30 cm^3) with stirring over 15 min. The mixture was stirred for 4 h the solid isolated by filtration, washed with diethylether and dried *in vacuo* at room temperature. The procedure was modified for (4,4'-bipyrH)$(VOCl_2(OCH_3))$, which required a reaction period of 5 min only, and $(trenH_2)(VOCl_2(OCH_3))_2$ which required a reaction period of 3 dy, but only 0.002 mol of ligand.

2. Procedure as for 1, but with a mole ratio $VOCl_2$, $3CH_3OH$: ligand = 1:4, in ether and a reaction period of 2 dy. $VOCl_2$, 3(3-mpy) was prepared using a mixture of 3-methylpyridine (15 cm^3) and diethylether (15 cm^3).

3. $VOCl_2.3CH_3OH$ (0.01 mol) was allowed to react with neat ligand (20 cm^3) for 1 wk and the product formed isolated as in 1. The species $VOCl_2$2L (L = a monomethylpyridine or pyridine) was obtained by heating $VOCl_2$,3L in vacuo. Similarly $VOCl_2,CH_3OH$,dmp.

4. Preparation of $VOCl(OCH_3)$,2py,LHCl (L = Et_3N, Et_2NH) $(LH)(VOCl_2(OCH_3))$ (0.01 mol) was alloved to react with pyridine (0.03 mol) in diethylether for 2 dy and the product isolated as above.

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(11) J. Selbin, *Chem. Rev.*, 1965, *65*, 153.