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Abstract

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TRIS(TRIORGANOSILYL)VANADATES

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Organic derivatives of vanadium have been studied very little. This is explained, above all, by the fact that this element, having valence electrons of different principal quantum numbers ($3d^3 4S^2$), is not inclined to form stable organic compounds with a vanadium—carbon bond (^{1}). However, compounds in which the vanadium atom is connected with carbon through oxygen have also been described quite insufficiently in the literature (^{2}).

In the present work we have studied the possibility of synthesizing organosilicon derivatives of vanadium containing the V—O—Si bond, tris(triorganosilyl)vanadates, hitherto unknown. These compounds were obtained by us by the interaction of triorganosilanols with V_2O_5, $VOCl_3$, or trialkyl vanadates $OV(OR)_3$, and also by the reaction of sodium triethylsilanolate with $VOCl_3$.

The simplest method for preparing tris(triorganosilyl)vanadates is the reaction of vanadium pentoxide with triorganosilanols:

$$6R_3SiOH + V_2O_5 leftarrows 2(R_3SiO)_3VO + 3H_2O, \tag{1}$$

carried out under conditions in which the water formed is removed by continuous azeotropic distillation. Benzene or another suitable solvent is used as the second component of the azeotropic mixture. Distillation of the water makes it possible to shift the reaction equilibrium toward formation of tris(triorganosilyl)vanadates, the yields of which are 50-80%.

Another simple method for synthesizing triorganosilyl esters of orthovanadic acid is based on the reaction of vanadium oxychloride with triorganosilanols in the presence of acceptors of hydrogen chloride (ammonia, tertiary amines, etc.):

$$3R_3SiOH + VOCl_3 + 3B \rightarrow (R_3SiO)_3VO + 3B \cdot HCl, \tag{2}$$

where $B = NH_3$ (a); C_5H_5N (b).
The yield of esters in this case is 60-80%.

A convenient method for the synthesis of organosilicon esters of orthovanadic acid is the transesterification of trialkyl vanadates with triorganosilanols in the presence of catalytic amounts of the sodium derivatives of the latter (formed upon addition of metallic sodium):

$$3R'_3SiOH + (RO)_3VO \overset{R'{}_3SiO^-}{\longrightarrow} (R'_3SiO)_3VO + ROH, \tag{3}$$

where $R = C_2H_5$ (a), n-C_4H_9 (b); $R' = CH_3, C_2H_5, C_6H_5$. Earlier, an analogous reaction was successfully used by us for the synthesis of organosilicon esters of boric (3) and orthotitanic* (4) acids. The indicated reaction is carried out by distilling off from the mixture of components the alcohol formed during their interaction, after which the reaction product is isolated either by distillation in vacuum or by recrystallization. The yield of tris(triorganosilyl)vanadates reaches 90%.

Finally, tris(triorganosilyl)vanadates can be obtained from ···in good yields by the reaction of sodium triorganosilanolates with vanadium oxychloride according to the scheme:

$$3R_3SiONa + VOCl_3 \rightarrow (R_3SiO)_3VO + 3NaCl. \tag{4}$$

Tris(trialkylsilyl) vanadates are colorless, relatively mobile liquids with a faint odor of trialkylsilanols, readily soluble in organic solvents. Tris(triphenylsilyl) vanadate is a crystalline substance. It is interesting that the carbon analogue of tris(trimethylsilyl) vanadate–tert-butyl vanadate, obtained by us in 10% yield by the reaction of V_2O_5 with $(CH_3)_3 \cdot COH$, consists of colorless crystals with m.p. 48° and b.p. 128—130°/20 mm. All tris(triorganosilyl) vanadates are insoluble in water, but are hydrolyzed by it with formation of the corresponding silanols and orthovanadic acid. The tendency toward hydrolysis decreases as the size of the organic radical attached to silicon increases. It should be noted that the thermal stability of tris(triorganosilyl) vanadates is insufficient; however, it is higher than that of their organic analogues. Thus, for example, tris(diethylphenylsilyl) vanadate, on distillation in vacuo at 2 mm, decomposes to a considerable extent with formation of lower oxides of vanadium. Similarly, although to a lesser degree, other tris(triorganosilyl) vanadates behave.

The properties of the synthesized tris(triorganosilyl) vanadates are presented in Table 1.

Table 1

Tris(triorganosilyl) vanadates

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* Simultaneously with us, tetrakis(triorganosilyl)titanates were obtained by this method by other authors as well (5,6).

Compound	B.p., °C	Pressure, mm Hg	M.p., °C	d_4^{20}	n_D^{20}	Yield, %	Si, % found	Si, % calc.	V, % found	V, % calc.	Obtained according to scheme
$[(CH_3)_3SiO]_3VO$	118–120	18	–	0.9812	1.4542	43.3	25.19	–	15.23	15.25; 15.19	(1)
$[(CH_3)_2C_2H_5SiO]_3VO$	124–126	7	–	0.9802	1.4670	71.5	22.37	–	13.55	13.55; 13.49	(3)
$[(C_2H_5)_3SiO]_3VO$	165–170	5	–	0.9894	1.4730	38.6	20.31	20.06; 20.03	12.17	12.18; 12.02	(1)
[[unclear compound formula]]	189–192	6	–	0.9830	1.4808	81.0	18.29	18.12; 18.30	11.06	10.99; 11.00	(1)
[[unclear compound formula]]	182–185	5	–	0.9835	1.4828	94.0	18.29	18.11; 18.39	11.06	11.36; 11.13	(3)
$[(C_2H_5)_3SiO]_3VO$	198–201	13	–	0.9825	1.4820	76.0	18.29	18.15; 18.27	11.06	10.89; 10.82	(2) a
[[unclear compound formula]]	170–173	4	–	0.9837	1.4818	85.0	18.29	18.00; 18.16	11.06	10.87; 10.81	(4)
[[unclear compound formula]]	192–194	7	–	0.9816	1.4812	55.5	18.29	18.00; 18.36	11.06	11.02; 10.86	(2) a
$[(C_2H_5)_2C_6H_5SiO]_3VO$	266–268	1.5	–	0.0767	1.5485	46.0	13.93	14.92; 14.87	8.42	7.44; 7.53	(1)
$[(C_6H_5)_3SiO]_3VO$	–	–	228	–	N_g 1.689*; N_p 1.664	90.0	9.43	9.18; 8.86	5.70	5.51; 5.62	(3) b

* Determined by the immersion method.

Experimental Part

Starting reagents

V_2O_5 was a commercial preparation (analytical grade). $VOCl_3$ was obtained by the reaction of vanadium pentoxide with thionyl chloride (7), b.p. 126°/758 mm. Triethyl vanadate was synthesized by the reaction of absolute ethyl alcohol with···

$VOCl_3$ in the presence of ammonia and had b.p. 91°/11 mm; d_4^{20} 1.167; n_D^{20} 1.5103. Tri-*n*-butyl vanadate was obtained in 23% yield by boiling, under reflux with a water trap, a twofold excess of *n*-butyl alcohol with benzene and vanadium pentoxide, and had b.p. 154—156°/10 mm; d_4^{20} 1.0376, n_D^{20} 4915. The triorganosilanols were obtained by the method described earlier (4).

Analysis. Silicon was determined by wet combustion of a weighed sample of the substance with a mixture of oleum and nitric acid. The precipitate of silicic acid was filtered off and ignited at 900°. Vanadium was determined either by evaporating the filtrate with subsequent ignition at 900°, or by hydrolysis of a separate weighed sample with an acidified aqueous-alcoholic mixture, followed by evaporation of the solution and ignition of the V_2O_5 precipitate at 900°. The latter method was used in the analysis of the lower tris(trialkylsilyl) vanadates.

All the methods we developed for the synthesis of tris(triorganosilyl) vanadates according to schemes (1)–(4) are illustrated below by the preparation of tris(triethylsilyl) vanadate. The physical properties and analytical data for this compound, purified in each individual case by secondary distillation in vacuo, are given in Table 1. All the other tris(triorganosilyl) vanadates were obtained analogously, with the exception of tris(triphenylsilyl) vanadate, synthesized according to scheme (3) b in an *o*-xylene medium, from which it was recrystallized.

Synthesis according to scheme (1). A mixture of 3.64 g (0.02 mole) of V_2O_5, 15.9 g (0.12 mole) of triethylsilanol (b.p. 75°/24 mm, n_D^{20} 1.4340, d_4^{20} 0.8645), and 80 ml of benzene was heated to boiling under reflux connected to a water trap for 2 h. During this time about 1 ml of water was liberated. The reaction mixture was filtered, and the filtrate, after removal of benzene, was subjected to fractional distillation in vacuo. 15.0 g (81%) of tris(triethylsilyl) vanadate was obtained, with b.p. 188—192°/6 mm.

Synthesis according to scheme (2). a. Into a 500-ml three-necked flask equipped with a mechanical stirrer with a mercury seal, dropping funnel, reflux condenser, and gas outlet tube were placed 250 ml of benzene and 16.0 g (0.12 mole) of triethylsilanol. To this solution, with stirring and cooling, was added dropwise a solution of 7.0 g (0.04 mole) of $VOCl_3$ in 50 ml of benzene. At the same time, ammonia dried over solid KOH was passed through the reaction mixture. The addition was carried out over 1 h in such a way that the temperature of the reaction mixture did not exceed 8°. After all the $VOCl_3$ had been added, ammonia was passed for another 15 min. The reaction was completed by heating on a water bath for 1 h at 80°. The reaction mixture was filtered, and the filtrate, after removal of benzene, was fractionated in vacuo. The yield of tris(triethylsilyl) vanadate with b.p. 192—194°/7 mm was 10.0 g, or 54.5%.

b. To 16.0 g (0.12 mole) of triethylsilanol, 80 ml of benzene, and 8.7 g (0.11 mole) of pyridine, cooled to −2°, was slowly added a solution of 7.0 g (0.04 mole) of $VOCl_3$ in 30 ml of benzene, so that the temperature of the mixture did not exceed +3°. After addition of the entire $VOCl_3$ solution, the reaction mixture was heated for 2 h to 70—80°. After cooling, the reaction mixture was filtered, and the filtrate, after removal of benzene, was distilled in vacuo. 14.0 g (76%) of tris(triethylsilyl) vanadate was obtained, with b.p. 198—201°/13 mm.

Synthesis according to scheme (3). Into a flask with a Vigreux column were placed 6.1 g (0.032 mole) of triethyl vanadate, 13.2 g (0.1 mole) of triethylsilanol, and 0.005 g of metallic sodium. The mixture was slowly distilled until 4.0 g of ethyl alcohol had distilled over at 78—84°. Fractional vacuum distillation of the residue gave 13.0 g (94%) of tris(triethylsilyl) vanadate, with b.p. 182—185°/5 mm.

Synthesis according to scheme (4). To a solution of 16.0 g (0.12 mole) of triethylsilanol in 400 ml of benzene was added 2.76 g (0.12 g-at.) of metallic sodium. The mixture was boiled for 8 h, until all the sodium had dissolved. To the sodium triethylsilanolate thus obtained, with cooling by ice water and stirring, 6.9 g (0.04 g-mole) of $VOCl_3$ in 15 ml of benzene was added. The reaction mixture was then heated for 2 h to 70-80°. After separation of sodium chloride and removal of the benzene, the residue was subjected to fractional distillation in vacuum. 16.0 g (87%) of tris(triethylsilyl) vanadate was obtained, b.p. 184-194°/7 mm.

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