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SYNTHESIS AND PROPERTIES OF ALKOXY DERIVATIVES OF VANADIUM $R_2V(OR')_2$

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Summary

The interaction of R_4V (R = Me, Ph, CH_2Ph) with monoatomic alcohols R'OH (R' = Me, i-Pr, n-Bu, t-Bu) has been studied. It has been found that the stability of $(PhCH_2)_2V(OR')_2$ falls in the following sequence: t-BuO > i-PrO > n-BuO ⩾ MeO.

The interaction of R_4V with t-BuOH in the ratio 1 : 2 leads to the formation of stable compounds of the type $(t\text{-}BuO)_2VR_2$ (where R = Me, CH_2Ph). The compounds are characterized by elementary analysis, molecular weight and ESR spectra.

Introduction

At present alkoxy derivatives of titanium, of the type $R_nTi(OR')_{4-n}$ (where R is alkyl and aryl), have been investigated in detail, and have been shown to be thermally more stable than the corresponding R_nTiHal_{4-n} [1,2]. Only one covalent alkoxy derivative of vanadium $(Me)(i\text{-}PrO)_2VO$ is known, which was obtained by the exchange reaction of $Cl(i\text{-}PrO)_2VO$ with dimethylzinc [3]. In this work we studied the possibility of preparing alkoxy compounds of vanadium $R_nV(OR')_{4-n}$.

Results and discussion

In order to solve this problem we have studied: (a) Interactions $R_4V + n$ R'OH and $(R'O)_4V + n$ RMet; (b) Exchange reactions $Cl_nV(OR')_{4-n} + n$ RMgX.

The reactions of R_4V * (R = Me, Ph, CH_2Ph) with monoatomic alcohols R'OH (methyl, isopropyl, n-butyl and t-butyl alcohols) were carried out in ether and

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* Solutions of Ph_4V and Me_4V were used immediately after their formation at −70°C by reacting VCl_4 and RLi.

hexane solutions at low temperatures. The ratio of components was varied from 1 : 1 to 1 : 3. Due to these reactions the corresponding amount of hydrocarbon was isolated and mixed alkoxy derivatives $R_nV(OR')_{4-n}$ were obtained. Interactions of $(PhCH_2)_4V$ with the above alcohols in the ratio 1 : 2 allowed us to determine the thermal stability of alkoxy derivatives depending on the nature of OR' group, by using ESR. The formation of $(PhCH_2)_2V(OMe)_2$ can be observed only below −30°C as it decomposes instantly at 0°C, similar behavior is also characteristic of $(n\text{-}BuO)_2V(CH_2Ph)_2$. $(i\text{-}PrO)_2V(CH_2Ph)_2$ is more stable; it decomposes at 20°C after 5 h. $(t\text{-}BuO)_2V(CH_2Ph)_2$ proves to be the most stable; this compound does not decay at 20°C for several months, but it decomposes in ether solution at 90°C after 25 h. Thus, the stability of $(PhCH_2)_2V(OR')_2$, depending on an alkoxy substituent, decreases in the sequence: $t\text{-}BuO > i\text{-}PrO > n\text{-}BuO \geqslant OMe$.

Dimethyl- and diphenylvanadium di(t-butoxides) also prove to be much more stable than other dialkoxides and the corresponding tetracovalent derivatives. They are prepared by the interaction of R_4V with t-BuOH in the ratio 1 : 2.

$$R_4V + 2\,t\text{-}BuOH \rightarrow (t\text{-}BuO)_2VR_2 + 2\,RH \qquad (1)$$

(where R = Me, Ph, CH_2Ph).

The compounds formed are monomeric paramagnetic dark liquids which are extremely sensitive to oxygen and moisture. They are decomposed by water solutions of mineral acids as well as by gaseous hydrogen chloride.

$$(t\text{-}BuO)_2VR_2 + 4\,HX \rightarrow 2\,RH + 2\,R'OH + VX_4 \qquad (2)$$

However, interactions of methyl- and benzyldialkoxy derivatives of vanadium with an excess of t-BuOH proceed only on heating to 90°C and are accompanied by the cleavage of both R—V bonds with formation of tetrakis(t-butoxide)vanadium.

$$(t\text{-}BuO)_2VR_2 + 2\,t\text{-}BuOH \xrightarrow[2-3\,h]{90^\circ C} 2\,RH + V(t\text{-}BuO)_4 \qquad (3)$$

(where R = Me, CH_2Ph).

The temperature ranges of $(t\text{-}BuO)_2VR_2$ decomposition are determined by the DTA method. $(t\text{-}BuO)_2V(CH_2Ph)_2$ starts to decay above 100°C with maximum of exothermic effect at 152°C (heating rate 7°C per minute).

Decomposition of $(t\text{-}BuO)_2VMe_2$ begins at 77°C and proceeds spontaneously in the region of the exothermic effect at 136°C. $(t\text{-}BuO)_2VPh_2$ already decomposes slowly at room temperature, this hinders its isolation in the pure form. Consequently, the stability of dialkoxides $R_2V(OR')_2$, depending on the nature of the covalent substituent, changes in the sequence: $PhCH_2 > Me > Ph$.

The stability of $(t\text{-}BuO)_2VR_2$ can be explained by steric factors. Due to the geometric configuration of a t-butoxy group a vanadium atom is shielded, and the attacks of electrophilic and nucleophilic agents on it are hindered.

Ether solutions of $R_2V(OR')_2$ have an ESR spectrum typical of compounds of vanadium (IV), consisting of eight components of superfine structure which arise from the interaction of an unpaired electron with the nucleus of ^{51}V ($J = \frac{7}{2}$). The parameters of the isotropic ESR spectra of $R_2V(OR')_2$ in diethyl ether are given in Table 1.

The small variation in the isotropic parameters of the ESR spectra in the series of

TABLE 1

SUPERFINE INTERACTION CONSTANTS A_i^{51} AND g_i OF ESR SPECTRA FOR $R_2V(OR')_2$ IN ETHER

Compound	A_i^{51} (e) [a]	g_i [b]
$(t\text{-}BuO)_2VMe_2$	—(51.5)	1.9687
$(t\text{-}BuO)_2VPh_2$	—(47.9)	1.9730
$(t\text{-}BuO)_2V(CH_2Ph)_2$	—(48.7)	1.9711
$(i\text{-}PrO)_2V(CH_2Ph)_2$	—(49.5)	1.9710

[a] Error ± 0.3 e. [b] Error ± 0.0005.

compounds mentioned indicate the similarity of their molecular and electronic structure.

Investigations which were recently undertaken showed that the isotropic parameters of the ESR spectra for $(Me_3SiCH_2)_4V$ are A_i^{51} 53.5 e, g_i 1.968; for Nor_4V 99 e and 2.000 and for $(t\text{-}BuO)_4V$ 68 e and 1.964, respectively [4—6].

We have also studied the interaction of $(t\text{-}BuO)_4V$ with various alkylating agents; it did not react with Me_2Cd and $(PhCH_2)_2Mg$. The interaction of tetrakis(t-butoxide)vanadium with $PhCH_2MgCl$ is accompanied by reduction to vanadium(III). Only methylmagnesium bromide alkylates $(r\text{-}BuO)_4V$ up to $(t\text{-}BuO)_2VMe_2$.

$$(t\text{-}BuO)_4V + 2\ MeMgBr \xrightarrow{-10^\circ C} (t\text{-}BuO)_2VMe_2 + 2\ t\text{-}BuOMgBr \qquad (4)$$

Initial $(t\text{-}BuO)_4V$ was obtained in a good yield (70%) according to the reaction:

$$VCl_4 + 4\ t\text{-}BuOLi \xrightarrow[-70^\circ C]{Et_2O\ +\ hexane} (t\text{-}BuO)_4V + 4\ LiCl \qquad (5)$$

The method of $(t\text{-}BuO)_4V$ synthesis is much easier than those known in the literature [7], and we believe that it is worthy of note.

The exchange reaction of $(t\text{-}BuO)_2VCl_2$ with a Grignard reagent can also be employed for the synthesis of $(t\text{-}BuO)_2VR_2$ derivatives. Di(t-butoxide)vanadium dichloride was formed according to the equation:

$$VCl_4 + 2\ t\text{-}BuOLi \xrightarrow[-78^\circ C]{Et_2O\ +\ hexane} (t\text{-}BuO)_2VCl_2 + 2\ LiCl \qquad (6)$$

The compound is stable only up to —60°C; therefore the exchange reaction was carried out in the solutions at —78°C.

$$(t\text{-}BuO)_2VCl_2 + 2\ RMgX \xrightarrow{-78^\circ C} (t\text{-}BuO)_2VR_2 + 2\ MgClX \qquad (7)$$

(where R = Me, Ph; X = Cl, Br).

The attempts to prepare $(t\text{-}BuO)_3VMe$ by the interaction of $(t\text{-}BuO)_3VCl$ with MeMgBr were unsuccessful This reaction yielded the mixture of $(t\text{-}BuO)_4V$ and $(t\text{-}BuO)_2VMe_2$, probably caused by disproportionation of initial tris(t-butoxide)vanadium chloride.

Thus, all methods which we have suggested can be used for the preparation of dialkoxides $R_2V(OR')_2$.

Experimental

All reactions were carried out in an argon atmosphere or under vacuum. Radiospectrometric measurements were carried out by means of a EPA-2M spectrometer. As a standard for calibration of magnetic field, samples of Mn^{2+} in the crystal lattice of MgO were used; for measuring the g-factor values, the water solution of Fremy salt was used. On determination of the g-factor values the correction of the second order for term A^2 was taken into account.

Preparation of dimethylbis(t-butoxy)vanadium

(a) 24.0 mmol of VCl_4 in 70 ml of ether are slowly added dropwise to an ether solution of 96.0 mmol of MeMgBr in an argon atmosphere at −78°C with vigorous stirring. When the addition of the whole amount of VCl_4 is complete 48.0 mmol of cooled (oxygen-free) t-butyl alcohol in 50 ml of pentane are added slowly to the reaction mixture. After stirring at −78°C for one hour the temperature of the reaction mixture is increased gradually to 20°C. A violet solution of $(t\text{-}BuO)_2VMe_2$ is separated from magnesium salts by filtration, the solvents are removed under vacuum and 1.3 g (24% from the theoretical value) of $(t\text{-}BuO)_2VMe_2$ is isolated from the residue by recondensation into an ampoule cooled at −20°C. $(t\text{-}BuO)_2VMe_2$ is a blue-violet liquid, b.p. 35—40°C/0.1 mmHg. (Found: C, 53.10; H, 10.70; V, 22.20; Mol. wt (cryoscopy in benzene) 215. $C_{10}H_{24}VO_2$ calcd.: C, 52.87; H, 10.57; V, 22.45%; Mol. wt 227.) A solution of $(t\text{-}BuO)_2VMe_2$ (0.5 g, 2.2 mmol) in n-heptane is treated with an excess of HCl in dioxan, methane (4.4 mmol) and t-butyl alcohol (4.3 mmol) were identified by means of GLC analysis.

(b) An ether solution of 17.4 mmol of MeMgBr is added slowly to 8.7 mmol of $(t\text{-}BuO)_4V$ in hexane with stirring at −10°C. The colour of the reaction mixture changes from blue to blue-violet through brown. The solution is separated from the precipitate by filtration, the solvents removed under vacuum, and $(t\text{-}BuO)_2VMe_2$ distilled from the residue at 35—40°C/0.1 mmHg. Yield 0.6 g (30% from the theoretical value).

(c) 38.8 mmol of a hexane solution of t-BuOLi prepared from 1.4 g Li and 9.4 ml of t-butyl alcohol in hexane are added slowly to 2.0 ml (19.4 mmol) of VCl_4 in 70 ml of ether at −78°C with vigorous stirring. The colour of the reaction mixture turns from red-brown to black. The $(t\text{-}BuO)_2VCl_2$ formed is stable below −60°C, on increasing the temperature it readily decomposes. 38.8 mmol of MeMgBr in ether are slowly added to the reaction mixture at −78°C with vigorous stirring. After stirring the reaction mixture for 2 h its temperature is gradually increased to 20°C. The violet solution is filtered from magnesium salts, the solvents are removed under vacuum, and $(t\text{-}BuO)_2VMe_2$ is isolated from the residue by distillation at 35—40°C/0.1 mmHg. Yield 1.72 g (46% from the theoretical value).

Preparation of dibenzylbis(t-butoxy)vanadium

(a) 20.0 mmol of cooled t-butyl alcohol in 50 ml of n-hexane are poured out slowly into 4.0 g (8.0 mmol) of crystalline tetrabenzylvanadium at −10°C with stirring. The reaction mixture is stirred at −10°C for 2 h longer, and the temperature increased gradually to 20°C. The green hexane solution is filtered through a fritted glass filter No. 4, and the solvent removed under vacuum. Toluene (15.0 mmol) was detected in the condensate by GLC. Dibenzyl which is present in organovanadium compounds as an impurity is separated from a dark green viscous liquid residue. Dibenzylbis(t-butoxy)vanadium (3.0 g, 7.9 mmol) is isolated as a green liquid. (Found: C, 69.20; H, 8.15; V, 13.60. $C_{22}H_{32}VO_2$ calcd.: C, 69.70; H, 8.45; V, 13.45%).

(b) 39.0 mmol of VCl_4 in 50 ml of ether are slowly added drop by drop to an ether solution of 156.0 mmol of $PhCH_2MgCl$ at −10°C with stirring. After stirring for one hour 28.0 ml of dioxan and then 7.0 ml (75.0 mmol) of cooled t-butyl alcohol in 150 ml of pentane are added gradually to the reaction mixture at the same temperature. The reaction mixture is stirred at −10°C for one hour, then the temperature is gradually increased to 20°C and the mixture is allowed to stand overnight. After filtration a green solution is separated from the precipitate of magnesium salts, and the solvents are removed under vacuum. The GLC analysis gave 79.0 mmol of toluene in the condensate. The residue which is formed after recondensation is dissolved in n-pentane, and the solution is filtered through a fritted glass filter No. 4 to isolate a precipitate. After removal of the solvent 8.0 g of dark green viscous liquid containing the impurity $(PhCH_2)_2$ are obtained. Dibenzyl is removed under vacuum. Dibenzylbis(t-butoxy)vanadium is not distilled under vacuum and this makes its purification from dibenzyl difficult. 6.3 g (43% from the theoretical value) of $(t\text{-}BuO)_2V(CH_2Ph)_2$ is obtained. (Found: C, 70.60; H, 8.42; V, 13.00. $C_{22}H_{32}VO_2$ calcd.: C, 69.70; H, 8.45; V, 13.45%.)

Attempts at preparation of diphenylbis(t-butoxy)vanadium

(a) 19.5 mmol of VCl_4 in 50 ml of ether are added slowly to an ether solution of 78.0 mmol of PhLi at −78°C with stirring. After stirring for one hour, 78.0 mmol of cooled t-butyl alcohol in 30 ml of n-hexane are poured out slowly into the reaction mixture at this temperature. The temperature of the reaction mixture is increased gradually to 0°C. The colour of the solution changes from black to dark green and the precipitate of salts is separated from the solution by filtration. The solution contains paramagnetic $(t\text{-}BuO)_2VPh_2$. This compound is thermally instable at room temperature, therefore, it is difficult to isolate it in the pure form.

(b) An ether solution of 29.0 mmol of PhMgBr is slowly added to a solution of $(t\text{-}BuO)_2VCl_2$ prepared from 14.5 mmol of VCl_4 and 29.0 mmol of t-BuOLi at −78°C, with stirring. After stirring for one hour the temperature of the reaction mixture is gradually increased to 0°C and the originally black solution turns green. At this time an ESR signal characteristic of $(t\text{-}BuO)_2VPh_2$ is recorded.

Preparation of tetrakis(t-butoxy)vanadium

A solution of 76.0 mmol of t-BuOLi in petroleum ether is added slowly to a solution of 2.0 ml (19.0 mmol) of VCl_4 in 100 ml of ether at −78°C with stirring. After stirring for one hour the temperature of the reaction mixture is increased gradually to 20°C. It is filtered to separate the blue solution from the precipitate of LiCl, and the solvent is removed under vacuum. The residue is distilled at 90°C/0.1 mmHg to afford 4.6 g (69% from the theoretical value) of $(t\text{-}BuO)_4V$. (Found: V, 14.76. $C_{16}H_{36}VO_4$ calcd.: V, 14.87%.)

Attempts at preparation of methyltris(t-butoxy)vanadium

43.5 mmol of a hexane solution of t-BuOLi are poured out slowly into 1.5 ml (14.5 mmol) of VCl_4 in 50 ml of ether under cooling (−78°C) and vigorous stirring. The solution turns from red-brown to black in colour. When stirring for one hour was complete 14.5 mmol of MeMgBr in ether is added slowly to the reaction mixture at the same temperature. The reaction mixture is stirred for one hour longer, and the temperature is gradually increased to 20°C. The sediment is separated from the blue solution by filtration, and the solvents are removed under vacuum. The residue (1.5 g, 40% yield based on V) is a blue liquid, its distillation at 40—90°C/0.1 mmHg gives a mixture of $(t\text{-}BuO)_4V$ and $(t\text{-}BuO)_2VMe_2$.

A special experiment showed that the equimolecular mixture of $(t\text{-}BuO)_2VMe_2$ and $(t\text{-}BuO)_4V$ is distilled in the temperature range mentioned.

In a parallel experiment, 14.5 mmol of $PhCH_2MgCl$ in ether are slowly added to the reaction mixture, prepared from 14.5 mmol of VCl_4 and 43.5 mmol of t-BuOLi at −78°C with vigorous stirring. The mixture is stirred for one hour, and then the temperature is increased gradually to 20°C. The blue-green solution is filtered from salts, and the solvent is removed under vacuum. Distillation of the residue at 90°C/0.1 mmHg gives 1 g (2.9 mmol) of $(t\text{-}BuO)_4V$.

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