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SOME REACTIONS OF TETRABENZYLVANADIUM

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Summary

The thermal decomposition of tetrabenzylvanadium has been studied with the help of differential thermal analysis (DTA) and the decomposition products identified. The reaction of tetrabenzylvanadium with acetylene and cyclopentadiene proceeds with displacement of four benzyl groups with formation of toluene. As a result of the interaction of tetrabenzylvanadium with tolan bis(hexaphenylbenzene)vanadium was isolated. The ESR spectra of tetrabenzylvanadium and its decomposition products, in the temperature range from −178 to +20°C, have been studied in diethyl ether.

Introduction

In the last few years the interest in tetrabenzyltitanium and tetrabenzylzirconium derivatives has been considerably aroused due to their increased thermal stability in comparison with alkyl and aryl analogues. The same trend is observed in a series of organovanadium compounds of the type R_4V. The crystalline $(C_6H_5CH_2)_4V\cdot(C_2H_5)_2O$ described earlier [1], is the first example of a relatively stable vanadium(IV) compound with four V—C σ-bonds. In the present work we continue the study of the properties of tetrabenzylvanadium.

Results and discussion

We have worked out a modified preparative method for crystalline tetrabenzylvanadium. As a result of magnesium salts precipitation by dioxan in the form of dioxanates and extraction of tetrabenzylvanadium by n-heptane we obtained black, low-melting crystals of the complex of variable composition $(C_6H_5CH_2)_4V\cdot nO(C_2H_5)_2\cdot mC_4H_8O_2$, where $n \leqslant 1.0$; $m \leqslant 2.0$.

The samples of complexes of tetrabenzylvanadium, prepared by this modified method, do not show an ESR signal as a solid or in diethyl ether solution at 0°C. However, when the crystalline etherate of tetrabenzylvanadium is being cooled directly in the resonator of a radiospectrometer an ESR signal appears, the intensity of which increases as the temperature is lowered. The ESR spectrum has an intense solitary line with $g = 1.965 \pm 0.005$ and the width at the half-maximum height, $H \simeq 80$ e at −196°C. When warmed to room temperature the intensity of the signal again decreases to zero.

A similar reversible temperature dependence is characteristic for the solution of tetrabenzylvanadium in diethyl ether. In this case when the temperature reaches the boiling-point of liquid nitrogen we observe a multicomponent spectrum with strongly pronounced anisotropy of super-fine structure, typical for paramagnetic species in "glass".

The data obtained differ from those described [2] for pentane solutions of tetrabenzyivanadium. According to this report the ESR spectrum of tetrabenzylvanadium in pentane at room temperature is a well resolved octet ($g = 1.993$) which is due to super-fine interaction of an unpaired electron with the nucleus ^{51}V ($a(^{51}V) = 57$ e). The observed additional super-fine splitting of each of the eight compounds ($a = 3$ e) is related by the authors to the eight equivalent protons of the benzyl groups.

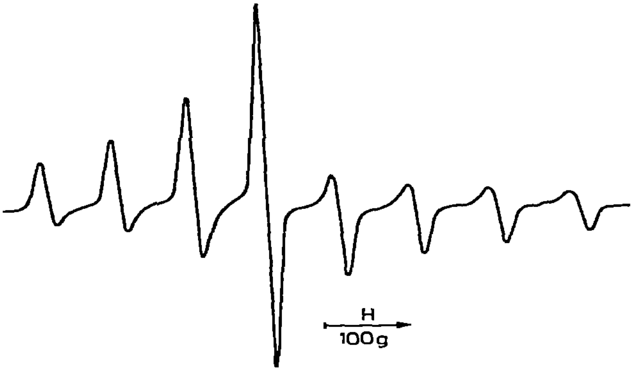
The ESR spectrum, with parameters close to those described in the paper by Ibekwe and Myatt [2] was observed for tetrabenzylvanadium in ether solution after only 3-5 min while keeping the sample at room temperature. More prolonged storage causes an increase in intensity of the ESR signal. The green colour of the solution, peculiar to tetrabenzylvanadium, simultaneously changes to brown. Warming acelerates thermal decomposition. The ESR spectrum of the paramagnetic product of thermal decomposition differs from tetrabenzylvanadium by its thermal stability and remains unchanged for several weeks. It is very sensitive to oxygen, the action of which causes the ESR signal to disappear together with simultaneous disappearance of the brown colour of the solution. The ESR anisotropic spectrum of this product registered in "glass-like" diethyl ether at the boiling temperature of nitrogen is shown in Fig. 1. Eight components of this spectrum belong to species the symmetry axis of which is perpendicular to the direction of the magnetic field $g_\perp = 1.977 \pm 0.004$; and $A_\perp = -94 \pm 1.0$.

The values $g_\parallel$ and $A_\parallel$ calculated from equations:

$$A_i = 1/3(A_\parallel + 2A_\perp),$$
$$g_i = 1/3(g_\parallel + 2g_\perp),$$

if $A_i < 0$ and $A_\perp < 0$, are correspondingly 2.004 and 0 e. The parameters of the ESR spectra obtained are very close to corresponding parameters of diarenevanadium(0) [3] and $(C_5H_5)V(C_7H_7)$ [4]. Thus we can propose that one of the thermal decomposition products of tetrabenzylvanadium is a diarenevanadium derivative.

The principal products after 12 h thermal decomposition of tetrabenzylvanadium in ether solution at 90°C are toluene (3.3-3.7 mol per mol of the primary product) and vanadium-containing solid residue, diamagnetic, black-brown powder with a temperature of decomposition > 150°C. Decomposition by acetic acid gave vanadium triacetate, gaseous hydrogen and small quantities of toluene. The total amount of toluene obtained in the process of thermal



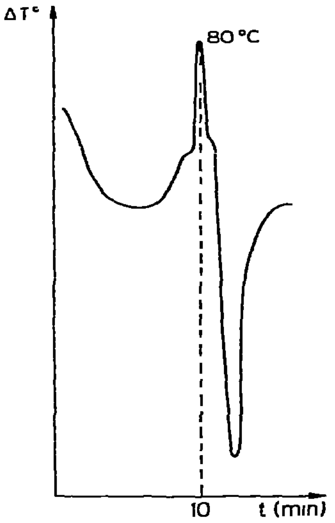


Fig. 1. The ESR anisotropic spectrum of diarenevanadium compound, registered in "glass-like" diethyl ether at the boiling temperature of liquid nitrogen.

Fig. 2. The curve of differential thermal analysis of the crystalline etherate of tetrabenzylvanadium.

and acidic decomposition was close to four. The balance in benzyl groups bound to an atom of vanadium in the primary compound indicates that ether is the source of hydrogen for formation of toluene. In the process of thermal decomposition of crystalline etherate $(C_6H_5CH_2)_4V \cdot n(C_2H_5)_2O \cdot m$ dioxan we observe a sharp decrease in the yield of toluene (up to 1.8-2.4 mol), dibenzyl ($\leqslant$ 0.3 mol) and vanadium-containing solid residue which gives in the process of acidolysis toluene, ether and dioxan. In this case diarenevanadium(0) was also identified by the ESR spectra of the reaction mixture. The course of thermal decomposition of the crystalline etherate of tetrabenzylvanadium is well illustrated by the differential thermal analysis curve (Fig. 2) from which it is evident that at room temperature, for a short period of time, elimination of ether is observed; at 80°C there is intensive decomposition with formation of toluene and other products. Since loss of crystallized ether occurs first, other benzyl groups must serve as the source of hydrogen that hinders thermal decomposition. Such processes were also noted with respect to benzylchromium derivatives [5].

In a number of published works formation of complexes of organo-titanium and -vanadium derivatives with acetylene and its substituted derivatives was mentioned [6,7]. In the present work we have examined the action of acetylene and diphenylacetylene on tetrabenzylvanadium.

When acetylene was passed through an ether solution of tetrabenzylvanadium at −10°C* there occurred immediate change of the colour of reaction mixture, displacement of 4 mol of toluene and deposition of a black-violet solid

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* It was shown by special experiments that at −10°C an ether solution of tetrabenzylvanadium remains stable over a week. The product of thermal decomposition of tetrabenzylvanadium does not interact with acetylene and tolan.

of acetylenides of vanadium. The coloured solid containing vanadium, carbon and hydrogen is oxidized in the air, decomposes without melting at above 300°C and does not dissolve in organic solvents. Another reaction product found was benzene (7.8 mol per mol of tetrabenzylvanadium). The formation of benzene is due to cyclotrimerization of acetylene on the transition metal atom. Thus acetylene reacts with tetrabenzylvanadium to give atoms of active hydrogen which in turn give four molecules of toluene.

In the reaction between tetrabenzylvanadium and diphenylacetylene, in ether solution at −10°C, we observed abstraction of benzyl groups with formation of toluene (0.6-1.0 mol) and dibenzyl (1.0 mol). The cyclotrimerization proceeding at the same time gives hexaphenylbenzene (2 mol per mol of vanadium). A paramagnetic, vanadium-containing, coloured product soluble in organic solvents was also detected. The ESR spectrum of this compound is characteristic for diarenevanadium derivatives ($g = 1.985 \pm 0.002$; $a(^{51}V) = 64$ e). After recrystallization from ether red-brown crystals were obtained melting at 110-112°C. In the course of acidolysis by acetic acid 1.6 mol of hexaphenylbenzene per mol of vanadium are formed. The data obtained indicate that one of the products of reaction between tetrabenzylvanadium and tolan is bis(hexaphenylbenzene)vanadium.

The reaction with cyclopentadiene also proceeded with displacement of 4 benzyl groups as toluene and probably formation of intermediate cyclopentadienylvanadium derivatives which on treatment with hydrogen chloride transform into $(C_5H_5)_2VCl$ and $(C_5H_5)_2VCl_2$ (in the presence of oxygen).

$$\begin{tikzcd}
(C_6H_5CH_2)_4V + 4\ C_5H_6 \arrow[r] & 4\ C_6H_5CH_3 + [(C_5H_5)_4V] \arrow[d] \\
& (C_5H_5)_3V + [C_5H_5^{\bullet}]
\end{tikzcd}$$

$$(C_5H_5)_3V \xrightarrow{HCl} (C_5H_5)_2VCl \xrightarrow{HCl + O_2} (C_5H_5)_2VCl_2$$

Experimental

The synthesis of tetrabenzylvanadium etherate

A solution of 0.03 mol VCl_4 in 70 ml ether was added dropwise, with stirring at −15°C to a suspension of 0.06 mol $(C_6H_5CH_2)_2Mg$ in 500 ml ether and 8 ml of dioxan. On completion of the addition the reaction mixture was stirred for 10 min 100 ml of cooled (oxygen free) n-heptane was added to the mixture. The green solution obtained was filtered from the $MgCl_2$-dioxanate residue and diethyl ether recondensed in the dark, under vacuum at a temperature ≤ −10°C. When the solution obtained was cooled to −78°C tetrabenzylvanadium slowly crystallized. The solution was decanted and the sediment $(C_6H_5CH_2)_4V \cdot n(C_2H_5)_2O \cdot m\, C_4H_8O_2$ dried under vacuum at 0°C (15-20% yield). $(C_6H_5CH_2)_4V \cdot n(C_2H_5)_2O \cdot C_4H_8O_2$ is a black, crystalline low-melting compound. (Found: C, 75.61; H, 7.21; V, 11.40. $C_{34}H_{41}VO_{2.5}$ calcd.: C, 75.50; H, 7.58; V, 10.18%.)

The complex (0.58 g, 0.94 mmol) was hydrolyzed by water acidified with H_2SO_4. Toluene (2.65 mmol), dibenzyl (0.57 mmol), dioxan (0.97 mmol) and small quantities of ether were detected.

The thermal decomposition of tetrabenzylvanadium in diethyl ether

The ether solution of tetrabenzylvanadium (5.90 mmol) was heated for 12 h at 90°C in an evacuated sealed ampoule. The colour of the solution changed from green to brown and a black precipitate was formed. The solvents were distilled under vacuo into a trap cooled by liquid nitrogen. In the condensate toluene (17.70 mmol) and benzene (0.04 mmol) were detected by gas-liquid chromatography (GLC). After the solvents had been removed the residue was subjected to acidolysis by glacial acetic acid. By means of the GLC method products detected were toluene (3.29 mmol), ether (0.35 mmol), dioxan (0.25 mmol), hydrogen (2.02 mmol), vanadium acetate (5.90 mmol) and oligomers (0.1 g).

In a parallel experiment, after the solvents were distilled under vacuo the residue was washed with ether and dried. Yield 1.2 g. (Found: V, 18.9%.) It is diamagnetic, black powder, pyrophoric in air with a decomposition point > 150°C.

The thermal decomposition of the crystalline tetrabenzylvanadium

Tetrabenzylvanadium etherate (2.5 g, 3.86 mmol) in an evacuated, sealed ampoule was kept in darkness at room temperature for 72 h after which the reaction mixture was heated for 2 h to form a dense dark brown liquid. The liquid fraction is evaporated under vacuo into a trap cooled by liquid nitrogen. Toluene (9.20 mmol), dioxan (4.05 mmol) and diethyl ether (1.71 mmol) were detected in the condensate by GLC.

After recondensation of the solvents the residue was subjected to acidolysis by glacial acetic acid. In the vapour phase was chromatographically determined hydrogen (0.34 mmol). In the condensate toluene (3.80 mmol), diethyl ether (0.30 mmol and dioxan (0.71 mmol) were determined. The residue after removal of acetic acid contains vanadium acetate* and traces of dibenzyl and oligomers (0.1 g, mol.wt. 400-500) insoluble in the saturated hydrocarbons but soluble in ether and benzene.

In a parallel experiment the product was isolated after washing the solid residue with ether. It is a diamagnetic black pyrophoric powder of unknown structure with decomposition temperature > 150°C. (Found: C, 69.93; H, 5.84; V, 18.22%.)

The reaction of tetrabenzylvanadium with acetylene

Acetylene was passed through an ether solution of tetrabenzylvanadium (0.75 mmol) at −10°C with stirring for 0.5 h (47.50 mmol of acetylene is absorbed, after primary absorption ceases). The solution becomes light brown and an abundant violet-black residue of acetylenides of vanadium precipitates. It is filtered, washed with ether and dried (0.62 g yield). (Found: C, 85.04; H, 5.86; V, 5.81%.) The product decomposes without melting > 300°C; in the air it oxidizes slowly to give a substance red-brown in colour. It is insoluble in organic solvents. In the filtrate toluene (3.00 mmol) and benzene (5.90 mmol) are determined by GLC.

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* Vanadium acetate (0.78 g; 1.10 mmol) was hydrolyzed with dilute solution of H_2SO_4. There was detected 3.25 mmol of CH_3COOH in the products of the hydrolysis; in the ratio $V/CH_3COOH = 1/3$.

Interaction of tetrabenzylvanadium with diphenylacetylene

An ether solution of tetrabenzylvanadium (2.62 mmol) was added to the cooled ether solution of diphenylacetylene (39.30 mmol) at −15°C. The colour of the solution changes from green to red-brown and over a longer period crystalline hexaphenylbenzene (3.38 mmol) precipitates. Hexaphenylbenzene melts at 420°C (lit. [8] 418°C). (Found: mol. wt. 510. $C_{42}H_{30}$ calcd.: 498.)

The solvent was recondensed under vacuo. In the condensate toluene (1.63 mmol) was detected by the GLC method. The red-brown residue was repeatedly washed with n-hexane; dibenzene (2.60 mmol) and unreacted tolane (16.60 mmol) were detected by GLC in the n-hexane. The resultant organovanadium compound $[C_6(C_6H_5)_6]_2V$ (1.39 g yield) is a reddish-brown powder soluble in benzene and ether and slightly soluble in n-hydrocarbons. Using the method of ether extraction we obtained $[C_6(C_6H_5)_6]_2V$ with m.p. 110-112°C. (Found: C, 89.70; H, 5.65; V, 4.60%; mol. wt. 1063. $C_{84}H_{60}V$ calcd.: C, 90.00; H, 5.35; V, 4.55%; mol. wt. 1119.) The compound is paramagnetic $g = 1.985 \pm 0.002$; $a(^{51}V) = 64$ e.

After acidolysis of 0.34 g (0.26 mmol) of $[C_6(C_6H_5)_6]_2V$ by acetic acid in the presence of oxygen $C_6(C_6H_5)_6$ was formed (0.20 g, 0.38 mmol), m.p. 420°C without depression.

Reaction of tetrabenzylvanadium with cyclopentadiene

An ether solution of cyclopentadiene (1.41 g, 24.40 mmol) was added to the ether solution of tetrabenzylvanadium (1.87 g, 5.93 mmol) at −15°C with vigorous stirring. The temperature of the reaction mixture was gradually increased to room temperature. The solvent was recondensed under vacuo. In the condensate toluene (23.50 mmol) was detected by the GLC method. To the residue we added benzene saturated with dry hydrogen chloride. The colour turns from brown to blue. Dicyclopentadienylvanadium(III) monochloride, intermediately formed, gave dicyclopentadienylvanadium(IV) dichloride by action of HCl and O_2. The green residue $(C_5H_5)_2VCl_2$ was filtered, washed with diethyl ether and dried. After recrystallization from chloroform we obtained 1.04 g (4.16 mmol) of $(C_5H_5)_2VCl_2$. (Found: V, 20.40; $C_{10}H_{10}VCl_2$ calcd.: V, 20.20%.)

The radiospectrometric measurements were taken using spectrometers RE-1301 and EPA-2 M. For thermostatting the sample in the resonator of the radiospectrometer we used the device TS-1 of the ICF of Academy of Sciences of the USSR. As a pattern for calibration of magnetic field we used the samples of Mn^{2+} in the crystal lattice of MgO. For measuring the values of g-factor the water solution of Fremy salt was used. When determining the values of g-factors we took into account the correction of the second order for term A^2.

All the samples investigated by the ESR method were released from dissolved gases by means of double degassing in vacuo.

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