Earlier,[5] we demonstrated experimentally the possibility of reaction (2) on oxide systems.

Propionitrile (**2**) can be obtained either directly from MeCN and MeOH

$$\mathrm{MeCN} + \mathrm{MeOH} \longrightarrow \underset{\mathbf{2}}{\mathrm{EtCN}} + \mathrm{H_2O}, \qquad (3a)$$

or by hydrogenating compound **1** formed at the stage (2) with hydrogen evolved in reaction (1)

$$\underset{\mathbf{1}}{\mathrm{CH_2{=}CHCN}} + \mathrm{H_2} \longrightarrow \underset{\mathbf{2}}{\mathrm{EtCN}}. \qquad (3b)$$

Stages (3a) and (3b) call for experimental confirmation, though some information concerning the possible hydrogenation of the double bond on metal oxides has been already published.[6]

References

1. A. L. Lapidus, M. M. Savel'ev, I. B. Kolesnikova, Kh. M. Minachev, N. Ya. Usachev, and O. N. Usacheva, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 2195 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 1721 (Engl. Transl.)].
2. A. L. Lapidus, M. V. Tsapkina, E. A. Kravtsova, B. P. Tonkonogov, and O. P. Lykov, *VIII Mezhdunar. konf. po khimicheskim reaktivam, Tez. dokl.* [*Abstr. of Papers, 8th Inter. Conf. on Chemicals*], Ufa—Moscow, 1995, 157 (in Russian).
3. In *Kataliticheskie svoistva veshchestv* [*Catalytical Properties of Substances*], Ed. V. A. Roiter, Naukova Dumka, Kiev, 1968, 589 (in Russian).
4. V. B. Kazanskii, *Problemy kinetiki i kataliza* [*Problems of Kinetics and Catalysis*], 1968, **12**, 217 (in Russian).
5. A. L. Lapidus, M. V. Tsapkina, E. A. Kravtsova, and E. G. Gorlov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 253 [*Russ. Chem. Bull.*, 1996, **45**, 244 (Engl. Transl.)].
6. O. V. Krylov, in *Kataliz nemetallami* [*Catalysis by Nonmetals*], Khimiya, Leningrad, 1967, 128 (in Russian).

Received November 29, 1996;
in revised form January 22, 1997

Destruction reactions of some σ-derivatives of vanadium

L. I. Vyshinskaya, S. P. Korneva, and G. P. Kulikova*

Scientific Research Chemistry Institute at N. I. Lobachevskii Nizhnii Novgorod State University,
23 prosp. Gagarina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: 007 (831 2) 35 6480

The interactions of $(Me_3SiCH_2)_4V$ and $(Me_3SiCH_2)_3V \cdot THF$ with cyclopentadiene have been studied. Me_4Si and Cp_2V were isolated. A scheme of the reactions was proposed which involves formation of unstable monocyclopentadienyl derivatives of vanadium.

Key words: cyclopentadiene, monocyclopentadienyl derivatives of vanadium.

At present, the reactivity of vanadium σ-derivatives of the types R_4V and R_3V (R = CH_2Ph, CH_2SiMe_3, C_6F_5, and MeS) has been little studied. The ability to cleave the M—C σ-bonds in the presence of compounds containing a mobile hydrogen is a common property for almost all σ-derivatives of transition metals. These reactions can be described by the general scheme

$$R_nM + nHX \longrightarrow nRH + MX_n.$$

The number of cleaved M—C σ-bonds depends on both the nature of the proton-active agent and the character of the σ-substituent.

Previously, we showed using the reaction of tetrabenzylvanadium with cyclopentadiene as an example that the V—C bond is cleaved to give dicyclopentadienylvanadium.[1] No formation of monocyclopentadienyl derivatives of vanadium was observed in this reaction.

In continuation of our investigations, we studied the interaction of tetrakis(trimethylsilylmethyl)vanadium and tris(trimethylsilylmethyl)vanadium tetrahydrofuranate with cyclopentadiene with different mole ratios of the starting components from 1 : 1 to 1 : 4. Complete disappearance of the vanadium(IV) ESR signal and the appearance of the ESR signal of dicyclopentadienyl derivative Cp_2V were observed as a result of the interac-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1542—1544, August, 1997.

tion of $(Me_3SiCH_2)_4V$ with CpH (in the 1 : 1 ratio, at 50 °C, 48 h). The volatile fraction was found to contain Me_4Si (>3 equiv.), while the residue was found to contain dicyclopentadienylvanadium and unidentified compounds of vanadium(II) (products of the decomposition of $(Me_3SiCH_2)_4V$). The same products and the unreacted cyclopentadiene (0.8 and 1.8 equiv., respectively) were isolated in the reactions of $(Me_3SiCH_2)_4V$ with CpH (in the 1 : 2 and 1 : 3 ratio).

The results obtained allowed us to suggest that one σ-bond is cleaved first and an unstable intermediate derivative $CpVR_3$ is formed (Scheme 1).

Scheme 1

$$(Me_3SiCH_2)_4V + CpH \xrightarrow{THF} Me_4Si + [CpV(CH_2SiMe_3)_3]$$

Similar to other XVR_3 (X = OR, Hal, OCOR, and acac), this derivative further decomposes to give a trivalent vanadium derivative $CpVR_2$ with subsequent disproportionation to Cp_2V and R_4V (Scheme 2).

Scheme 2

$$\begin{tikzcd}
{[CpVR_3]} \arrow[r] & {[CpVR_2]} \arrow[r] & 0.5\ Cp_2V + 0.5\ R_4V \arrow[d] \\
 & & V^{II} + RH
\end{tikzcd}$$

The results obtained indicate that irrespective of the nature of the substituent X, asymmetrical compounds of the tetravalent vanadium of the XVR_3 type are unstable under ordinary conditions and likely decompose instantly at the moment of their formation.[2] Previously, we established that the trivalent vanadium compounds of the R_2VX type (X = Hal, OR, OCOR, acac, and Cp) undergo intramolecular oxidation and reduction.[2] Introduction of a π-ligand into the molecule of an organovanadium compound has no substantial effect on the character of its transformations. The intermediate compound $[CpVR_3]$ that is formed decomposes faster than it can interact with the second cyclopentadiene molecule under the reaction conditions.

No monocyclopentadienyl derivatives of vanadium $CpVR_2$ were isolated in the case of interaction between tris(trimethylsilylmethyl)vanadium and cyclopentadiene (in 1 : 1 ratio). Tetramethylsilane, the unreacted cyclopentadiene, dicyclopentadienylvanadium, and products containing vanadium(II) and vanadium(III) were found among the reaction products.

The increase in the amount of tetramethylsilane obtained (from 0.9 to 1.6 equiv.) as the temperature increases from 20 to 50 °C can likely be explained by the decomposition of intermediate compounds that are formed under the reaction conditions (Scheme 3).

Scheme 3

$$\begin{aligned}
&(Me_3SiCH_2)_3V\cdot THF + CpH \longrightarrow \\
&\qquad \longrightarrow CpV(CH_2SiMe_3)_2 + Me_4Si \\
&\qquad\qquad \downarrow \\
&0.5\ Cp_2V + 0.5\ (Me_3SiCH_2)_4V \\
&\qquad\qquad\qquad \downarrow \\
&\qquad Me_4Si + \text{V-containing products}
\end{aligned}$$

Replacement of THF in $(Me_3SiCH_2)_3V\cdot THF$ by a bulkier ligand PEt_3 results in the formation of the complex $(Me_3SiCH_2)_3V\cdot PEt_3$, which does not react further with cyclopentadiene.

Experimental

All reactions were carried out in anhydrous solvents in the absence of moisture and air under a dry argon atmosphere, and GLC analysis was performed on a Tsvet-104 chromatograph. The ESR spectra were recorded on a RE-1301 instrument. Tri- and tetravalent vanadium derivatives were synthesized according to the known procedure.[2]

Reaction of tetrakis(trimethylsilylmethyl)vanadium with cyclopentadiene in a 1 : 1 ratio. Cyclopentadiene (0.13 g, 1.9 mmol) in 5 mL of THF was added to a solution of tetrakis(trimethylsilylmethyl)vanadium (0.78 g, 1.9 mmol) in 15 mL of THF at 20 °C, and the reaction mixture was kept at 50 °C for 48 h. The volatile fraction was recondensed *in vacuo*, and tetramethylsilane (0.51 g, 5.8 mmol, yield 76%) was identified in the condensate. Sublimation of the solid residue *in vacuo* gave dicyclopentadienylvanadium (0.16 g, 0.9 mmol). M.p. 168 °C, sublimation point 100 °C (1 Torr).[3] Found (%): C, 66.50; H, 5.58; V, 27.92. $C_{10}H_{10}V$. Calculated (%): C, 66.36; H, 5.50; V, 28.14. Low-valent organic derivatives of vanadium (0.9 mmol) in the residue were determined using the known procedure.[4]

Reaction of tris(trimethylsilylmethyl)vanadium tetrahydrofuranate with cyclopentadiene in a 1 : 1 ratio. *A. T* = 20 °C. Cyclopentadiene (0.40 g, 6 mmol) was added to a solution of tris(trimethylsilylmethyl)vanadium tetrahydrofuranate (2.3 g, 6 mmol) in 20 mL of THF at 20 °C, and the reaction mixture was kept at 20 °C for 48 h. The volatile fraction was recondensed, and tetramethylsilane (0.47 g, 5.4 mmol, yield 90%) was identified in the condensate. Sublimation of the solid residue *in vacuo* gave dicyclopentadienylvanadium (0.36 g, 2 mmol).

B. T = 50 °C. Cyclopentadiene (0.51 g, 7.8 mmol) was added to a solution of tris(trimethylsilylmethyl)vanadium tetrahydrofuranate (2.99 g, 7.8 mmol) in 20 mL of THF, and the reaction mixture was kept at 50 °C for 10 h. The volatile fraction was recondensed *in vacuo*, and tetramethylsilane (1.10 g, 12.5 mmol) was identified in the condensate.

Reaction of tris(trimethylsilylmethyl)vanadium tetrahydrofuranate with triethylphosphine. Triethylphosphine (0.7 g, 6 mmol) was added to a solution of tris(trimethylsilylmethyl)vanadium tetrahydrofuranate (2.3 g, 6 mmol) in 20 mL of THF at −20 °C. The temperature was raised to 20 °C, and the reaction mixture was kept for 48 h. The volatile fraction was recondensed, cyclopentadiene (0.4 g, 6 mmol) in 20 mL of THF was added to the residue, and the mixture was kept for 48 h at ~20 °C. The unreacted cyclopentadiene (5.4 mmol) was found by GLC in the volatile fraction. The solvent was removed from the reaction mixture *in vacuo*, and the solid residue was extracted with pentane. Cooling to −25 °C resulted in the precipitation of violet-brown crystals of $(Me_3SiCH_2)_3V \cdot PEt_3$ (1.83 g, yield 71%). Found (%): C, 49.86; H, 11.06; V, 11.35. $C_{18}H_{48}PSi_3V$. Calculated (%): C, 50.23; H, 11.16; V, 11.86.

References

1. G. A. Razuvaev, V. N. Latyaeva, L. I. Vyshinskaya, A. N. Lineva, V. V. Drobotenko, and V. K. Cherkasov, *J. Organomet. Chem.*, 1975, **93**, 113.
2. G. A. Razuvaev, V. N. Latyaeva, L. I. Vyshinskaya, and V. V. Drobotenko, *J. Organomet. Chem.*, 1981, **208**, 169.
3. E. O. Fischer and S. Vigoureux, *Chem. Ber.*, 1958, **94**, 2205.
4. V. N. Latyaeva, A. N. Lineva, L. I. Vyshinskaya, V. V. Drobotenko, and G. Ya. Mal'kova, *Khimiya elementoorgan. soedinenii, Mezhvuz. sb.* [*Chem. of Organoelem. Compds., Inter-Higher School Collect. of Works*], Gor'kovskii Gosudarstvennyi Universitet, Gor'kii, 1977, 5, 103 (in Russian).

Received December 3, 1996;
in revised form April 21, 1997

Separation of C_{60} and C_{70} fullerenes on silica modified by polyaromatic and π-acid aromatic compounds

L. L. Gumanov,[a] *B. L. Korsounskii,*[a]* *V. P. Bubnov,*[a] *E. B. Yagubskii,*[a] *and L. S. Pomogaeva*[b]

[a]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: 007 (096) 515 3588
[b]*Institute of Organic Intermediates and Dyes,*
1/4 ul. B. Sadovaya, 103787 Moscow, Russian Federation.
Fax: 007 (095) 408 7872

Separation of C_{60} and C_{70} fullerenes by HPLC was studied using sorbents synthesized by reaction of perylenedicarboxylic anhydride, dimethoxyviolanthrene, the tetramer of chromotropic acid with formaldehyde (TCA), trinitrobenzoyl chloride, or chlorotrinitrobenzene with γ-aminopropyl silica. These sorbents possess satisfactory chromatographic properties. The sorbent based on TCA is effective for separation of preparative amounts of fullerenes.

Key words: fullerenes, HPLC, sorbents.

The sorbents used currently for the separation of fullerenes by liquid chromatography are materials based on polyaromatic compounds bound to silica gel,[1] materials based on aromatic π-acids,[2] and sorbents based on porphyrins and phthalocyanines bound to silica gel.[3,4] A sorbent containing ethylpyrene linked to silica gel by covalent bonds belongs to the first group. Sorbents with grafted π-acids have been synthesized using dinitrofluorobenzene, which is a weak π-acid. In order to extend the range of materials suitable for separation of C_{60} and C_{70}, we prepared sorbents by reaction of various compounds with γ-aminopropyl silica gel (γ-APS). These compounds include stronger π-acids, *viz.*, trinitrobenzoyl chloride (sorbent **1**) and chlorotrinitrobenzene (sorbents **2** and **3**), and also substances characterized by larger effective areas of molecules than pyrene, *viz.*, perylenedicarboxylic acid anhydride (sorbent **4**), dimethoxyviolanthrene (sorbent **5**), and the tetramer of chromotropic acid with formaldehyde (TCA) (sorbent **6**).

Experimental

Sorbents **1**—**6** were synthesized using Separon-NH_2 γ-APS and poly-γ-APS; the latter was prepared by refluxing a dry sample of Separon-SGX silica gel with 15% γ-aminopropyltriethoxysilane and 15% water in toluene for 6 h followed by washing with isopropyl alcohol and drying *in vacuo*.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1544—1546, August, 1997.