# Reactions of vanadocene and its monochloride with *p*-toluenesulfonyl chloride

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The reactions of $Cp_2V$ and $Cp_2VCl$ with *p*-toluenesulfonyl chloride were studied. Depending on the ratio of the reagents, the solvent, and other reaction conditions, the compounds *p*-$MeC_6H_4SO_2VCp_2Cl$, (*p*-$MeC_6H_4SO_2VCp)_n$ or (*p*-$MeC_6H_4SO_2VO)_m$ are formed.

**Key words:** vanadocene, *p*-toluenesulfonyl chloride, interaction.

The reactions of vanadocene and its monochloride with *p*-toluenesulfonyl chloride were studied in continuation of the works[1—6] on studying the reactions of vanadium $\eta^5$-cyclopentadienyl derivatives with halogen- and sulfur-containing compounds and to extend the series of biologically active organometallic compounds resistant to oxidation.

In the absence of a solvent (in an evacuated sealed tube), vanadocene reacts very actively with *p*-toluenesulfonyl chloride at any ratio of the reagents, and the reaction begins even when the solid reagents cooled to the boiling point of liquid nitrogen are mixed. The process is accompanied by the strong heating of the mixture and formation of cyclopentadiene (CpH). The reaction products are sintered to form a greenish-brown mass, whose main identified component is vanadocene dichloride ($Cp_2VCl_2$). The attempts to obtain any other individual vanadium-containing compounds under these conditions were unsuccessful.

When the reaction is performed in benzene with a ratio of the reagents 1 : 1 (the gradual addition of a $Cp_2V$ solution to a solution of *p*-toluenesulfonyl chloride frozen at the liquid nitrogen temperature and then exposure for 24 h at 20—25 °C), the violet initial solution of vanadocene rapidly turns light-green, followed by the formation of the addition product of *p*-toluenesulfonyl chloride to vanadocene, bis($\eta^5$-cyclopentadienyl)vanadiumchloro-*p*-toluene sulfinate (**1**), which precipitates as green crystals, and $Cp_2VCl_2$ is present as an impurity.

$$p\text{-}MeC_6H_4SO_2Cl + Cp_2V \xrightarrow{LH} \underset{\mathbf{1}}{p\text{-}MeC_6H_4SO_2VCp_2Cl} \quad (1)$$

(LH is the hydrogen-containing solvent)

The dynamics of reaction (1) was controlled by ESR spectroscopy. Two eight-component signals were observed in the ESR spectrum immediately after mixing of solutions (~$2 \cdot 10^{-2}$ mol $L^{-1}$) of equimolar amounts of the reagents. Judging from the parameters $g_i$ = 1.9875 and $a_i(^{51}V)$ = 7.38 mT (73.8 Oe), one of them belongs to vanadocene dichloride.[7] Another signal, whose intensity at the initial stage of the reaction is threefold higher than that of the signal of $Cp_2VCl_2$, was assigned to complex **1**. The values of the parameters of the isotropic ESR spectrum observed, $g_i$ = 1.9817 and $a_i(^{51}V)$ = 7.63 mT (76.3 Oe), agree with the suggested structure of complex **1**, which is the product of the oxidative addition of *p*-toluenesulfonyl chloride to vanadocene. An increase in the $a_i(^{51}V)$ value and a decrease in $g_i$ compared to the corresponding spectral parameters of $Cp_2VCl_2$ are probably related to an increase in the positive charge on the V atom in a molecule of **1** compared to $Cp_2VCl_2$, which occurs when chlorine is substituted for the more electronegative toluenesulfonyl group.[7]

The subsequent changes in the ESR spectra also agree with the suggested assignment of the second signal. Its intensity decreases in time, and the intensity of the signal of $Cp_2VCl_2$ increases. After 48 h from the beginning of the reaction, the ratio of the intensities of the ESR spectra of complex **1** and $Cp_2VCl_2$ is 1 : 3, and after 168 h it is 1 : 10.

It is noteworthy that if the reaction takes place in toluene or without freezing of one of the reagents and a change in the order of their mixing (the addition of a solution of *p*-toluenesulfonyl chloride to vanadocene) it also favors a decrease in the intensity of the signal of compound **1** and an increase in the intensity of the signal of $Cp_2VCl_2$ in the ESR spectra (THF, toluene) of the resulting precipitates.

Starting from the experimental data considered, the accumulation of $Cp_2VCl_2$ in the reaction mixture can be explained, in our opinion, by the fast subsequent reactions involving initial *p*-toluenesulfonyl chloride and $Cp_2V$.

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These mutual transformations should be accompanied by the partial decomposition of the substances formed.

The first confirmation of this assumption is the isolation of ($\eta^5$-cyclopentadienylvanadium)-*p*-toluene sulfinate (**2**) (yield up to 15 %) from the mixture of the reaction (1) products. Compound **2** could be obtained only through the elimination of the Cp fragment with the participation of the second vanadocene molecule.

$$1 + Cp_2V \xrightarrow[-Cp_2VCl]{} [p\text{-}MeC_6H_4SO_2VCp_2] \xrightarrow[-CpH]{LH} p\text{-}MeC_6H_4SO_2VCp \quad (2)$$

**2**

Then it was established that compound **2** becomes the main product (yield ~70 %; the admixture of $Cp_2VCl_2$ was detected by the ESR method), and the dark-blue filtrate contains $Cp_2VCl$ (yield 60 %) as well, when the $Cp_2V$/*p*-toluenesulfonyl chloride ratio is 2 : 1 (benzene, 20—25 °C, 24—48 h).

$$1 + Cp_2V \xrightarrow[-Cp_2VCl]{} [p\text{-}MeC_6H_4SO_2VCp_2] \xrightarrow[-CpH]{LH} p\text{-}MeC_6H_4SO_2VCp \quad (3)$$

**2**

Finally, the change of benzene for toluene (presumably, the effect of specific solvation) results in the complete transformation of $Cp_2VCl$ into $Cp_2VCl_2$.

$$1 + Cp_2VCl \xrightarrow[-Cp_2VCl_2]{LH} 2 \quad (4)$$

It is noteworthy that compound **1** и $Cp_2VCl_2$ cannot be separated in the case when they form together, because their solubilities in organic solvents are close, and complex **1** is very unstable.

Special experiments show that under the conditions considered *p*-toluenesulfonyl chloride itself reacts with vanadocene monochloride according to Eq. (5) (benzene, toluene, yields of the products up to 80 %), and some amount of compound **2** is formed as well.

$$p\text{-}MeC_6H_4SO_2Cl + 2\ Cp_2VCl \xrightarrow[-Cp_2VCl_2]{LH} 1 \quad (5)$$

At the same time, we found that under the same conditions (the optimum conditions are THF, 20—25 °C, 24 h, yields of the products are 80—90 %) vanadocene can react with *p*-toluenesulfonyl chloride at the ratio of the reagents of 3 : 2 according to Eq. (6).

$$p\text{-}MeC_6H_4SO_2Cl + 1.5\ Cp_2V \xrightarrow[-CpH,\ -0.5\ Cp_2VCl_2]{LH} 2 \quad (6)$$

Compound **2** transforms very rapidly into vanadyl-*p*-toluene sulfinate (**3**) in air.

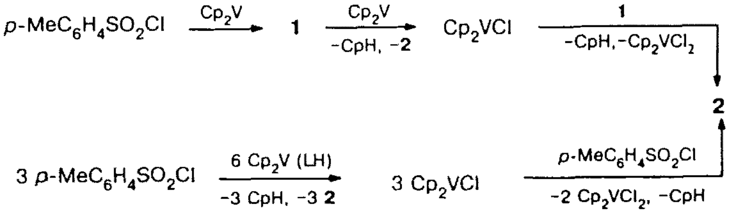
$$\underset{\mathbf{2}}{p\text{-}MeC_6H_4SO_2VCp} \xrightarrow[-CpH]{H_2O\ (O_2)} \underset{\mathbf{3}}{p\text{-}MeC_6H_4SO_2V{=}O} \quad (7)$$

Compounds **2** and **3** manifest no signals in the ESR spectra (THF, benzene, toluene).

Starting from the results considered above, the general scheme of the transformations of vanadocene under the action of *p*-toluenesulfonyl chloride can be presented as Scheme 1.

The products of reaction (1) were studied by the DTA method (Fig. 1). A considerable exothermic effect related likely to the decomposition of compound **1** was observed for all samples beginning from 75—80 °C. In the process of a further temperature increase, the samples studied in sealed or open crucibles manifest one or two endothermic transitions, respectively, surface areas under which make it possible to estimate relative amounts of the compounds. The temperature transition at 190—200 °C (see Fig. 1, thermograms *1—3*) can be assigned to the melting of the eutectic mixture of $Cp_2VCl_2$ and unreacted compound **1**. This considerable decrease in the melting point of $Cp_2VCl_2$ in the presence of admixtures of **1** compared to that of the individual substance (thermogram *5*, m.p. 232 °C) is likely related to the formation of solid solutions of these compounds with the isomorphous structure. The temperature endo-transition at 135—145 °C of the samples exposed in air can be assigned to the melting of

Scheme 1



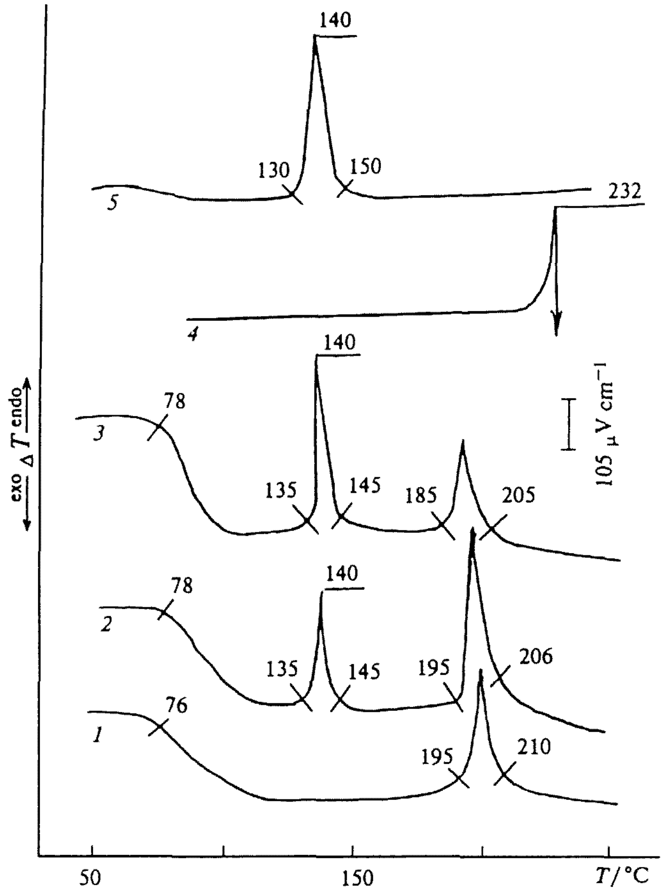


**Fig. 1.** DTA curves of the samples studied: *1*, a mixture of complex **1** and $Cp_2VCl_2$ in the sealed evacuated crucible; *2*, *3*, mixtures of compounds **1**, **3**, and $Cp_2VCl_2$ in open crucibles (synthesized in benzene (*2*) and toluene (*3*)); *4*, $Cp_2VCl_2$; *5*, compound **3**.

newly formed compound **3**. The temperature transitions of pure vanadyltoluene sulfinate **3** are presented in thermogram *4*.

The attempts to determine the DTA parameters of individual compounds **1** and **2** were unsuccessful due to technical difficulties associated with the preparation of samples for the analysis.

The analysis of the IR spectra of complexes **1**—**3** allows one to suppose that the decrease in the absorption frequencies of the $SO_2$ groups compared to the known values (for example, for $PhSO_2NH_2$) can be explained by the formation of strong coordination bonds of the V atoms with the O and S atoms of the corresponding dimeric or polymeric structures of the type $(p\text{-}MeC_6H_4SO_2VCp)_n$, $(p\text{-}MeC_6H_4SO_2V{=}O)_m$.

## Experimental

All chemical procedures were carried out in evacuated apparatus or sealed evacuated two-chambered tubes provided with glass filters.

IR spectra were recorded on a Specord-75-IR spectrophotometer (thin films of a substance in Vaseline oil between plates of KBr). ESR spectra were recorded on a Bruker-ER-200D-SRC instrument in the X-range (9.4 GHz). The temperatures of physical transitions were determined by the DTA method using a setup based on PRT-1000 M; the measurement error did not exceed 0.7 %, the heating velocity was 5 or 10 °C per min, and the sensitivity of thermocouples was 6.9 mV $cm^{-1}$.

**Bis($\eta^5$-cyclopentadienyl)vanadiumchloro-*p*-toluene sulfinate (1).** A solution of vanadocene (0.66 g) in benzene (20 mL) (the ratio of the reagents was 1 : 1) was added to a solution of *p*-toluenesulfonyl chloride (0.70 g) in benzene (20 mL) frozen at the liquid nitrogen temperature. As the reaction solution was frozen out to room temperature, its color changed from violet to greenish-brown. The mixture was kept for 48 h at ~20 °C, and the green precipitate was filtered off, washed with benzene, and dried *in vacuo*. According to the data of ESR spectroscopy (THF, benzene), the resulting compound (0.90 g) was a mixture of approximately equal amounts of compound **1** ($a_i(^{51}V)$ = 76.8 Oe, $g_i$ = 1.9817) and $Cp_2VCl_2$ ($a_i(^{51}V)$ = 73.8 Oe, $g_i$ = 1.9875). IR spectrum of complex **1**, ν/$cm^{-1}$: 3100, 1600, 1090, 1060, 1015, 970, 830, 690, 645, 630, 550 (C—H arom. of Ph- and Cp-cycles); 1235, 1130 ($SO_2$).

The solvent was removed from the brown filtrate. The resin-like dark-brown precipitate of compound **2** (0.2 g), which was separated from the walls only upon deep cooling (liquid nitrogen), remained in the tube.

**($\eta^5$-Cyclopentadienyl)vanadium-*p*-toluene sulfinate (2).** $Cp_2V$ (1.05 g) was added to a solution of *p*-toluenesulfonyl chloride (0.74 g) in THF (40 mL) (the ratio of the reagents was 2 : 3). During thawing, the solution changed its color from violet *via* green to brown. The reaction mixture was kept for 24 h at ~20 °C. The solvent was removed from the brown filtrate (obtained after separation of $Cp_2VCl_2$ formed) by recondensation *in vacuo*. Compound **2** (1.41 g, 89 %) was obtained as dark-brown lustrous flakes, which spread over the inner surface of the tube on slight heating. Compound **2** is soluble in THF, benzene, and toluene and insoluble in hexane. Found (%): C, 53.91; H, 4.82; S, 12.55; V, 18.03. $C_{12}H_{12}O_2SV$. Calculated (%): C, 53.14; H, 4.43; S, 11.81; V, 18.82. CpH was determined quantitatively by GC. IR, ν/$cm^{-1}$: 3070, 1075, 1020, 820, 805, 670, 570 (C—H arom. of Ph and Cp cycles); 1260, 1110 ($SO_2$).

**Vanadyl-*p*-toluene sulfinate (3).** An evacuated tube containing a solution of compound **2** (0.60 g) in benzene was opened and kept for 24 h in air at ~20 °C. The dark-brown fine precipitate was filtered off to obtain compound **3** (0.42 g, 94 %) with m.p. 135—140 °C (DTA). Found (%): C, 37.92; H, 3.33; V, 22.77. $C_7H_7O_3SV$. Calculated (%): C, 37.85; H, 3.18; V, 22.91. IR, ν/$cm^{-1}$: 3090, 1005, 830, 675, 570 (C—H of Ph cycle); 1260, 1120 ($SO_2$); 1035 (V=O).

The reaction of compound **3** with HCl in dioxane gives $VOCl_2$. ESR (THF)[5]: $a_i(^{51}V)$ = 108.0 Oe.

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