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Formation of a Cluster $H_2V_{10}O_{28}^{4-}$ under the Action of Brønsted Acids and Its Catalytic Activity in Oxidation of Alkylbenzenes

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Abstract—New method was developed for the preparation of vanadium cluster of the composition $\{Me_2NH_2\}_4$* $H_2V_{10}O_{28}$ from vanadyl(IV) acetylacetonate in the presence of 2-hydroxy-2-trifluoromethylchroman-4-one or its synthetic precursor, 2'-hydroxyacetophenone. The structure of the cluster was proved by X-ray diffraction (XRD) analysis. The cluster of decavanadate catalyzes oxidation of toluene and *o*-xylene creating promising situation for developing new catalytic materials.

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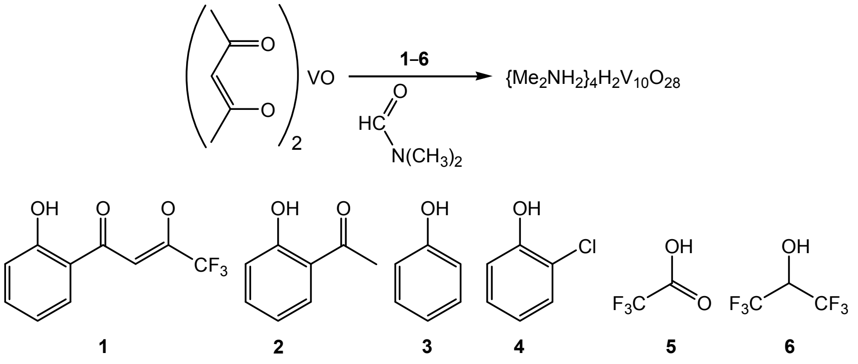
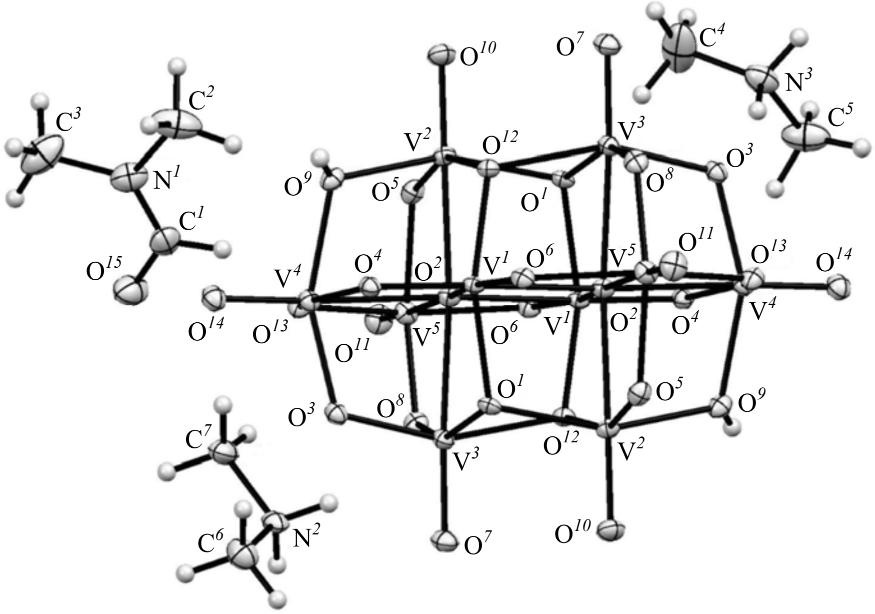
Coordination compounds of transition metals play important role in various transformations of organic compounds [1]. Considering also the enzymatic function of complexes it should be mentioned that they take part in biomimetic [2, 3], heterogenic [4, 5], homogenous [5, 6], in particular, template [7] catalysis and are as well used as reagents [8]. Therewith the cluster organization of complexes in some cases is more preferable than the mononuclear structure [9].

Decavanadate cluster of the composition $V_{10}O_{28}^{6-}$ due to its high thermodynamic stability forms in a wide range of synthetic conditions from various inorganic compounds [10–12] and in the presence of diverse organic bases [13–17]. The wish to obtain the decavanadate is due to its biochemical [13, 18], pharmacological [14–17], and catalytic [10, 19–21] activity. Although the decavanadate is already known for a long time, its applicability to the catalysis of organic reactions is poorly studied [10, 19–21]. This research consisted in development of a new method of decavanadate cluster preparation and estimation of its opportunity to be used as heterogenic catalyst of toluene and *o*-xylene oxidation.

Systematic examination of complex forming properties of 2-hydroxy-2-trifluoromethylchroman-4-one with ions of copper (II), nickel(II), and cobalt(II) showed the high activity of the ligand similar to that of 1,3,5-triketones, also at the formation of binuclear complexes [22]. In this study the attempt to obtain with this ligand a complex with the vanadyl(IV) ion unexpectedly led to the formation of a cluster $H_2V_{10}O_{28}^{4-}$ (Scheme 1).

Scheme 1.





Molecular structure of tetradimethylammonium dihydro-decavanadate(V) represented in thermal ellipsoids of 50% probability.

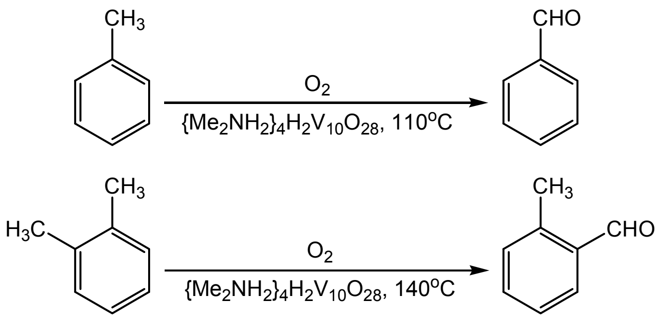
The reaction of 2-hydroxy-2-trifluoromethylchroman-4-one with vanadyl(IV) acetylacetonate was carried out in DMF. As a result orange crystals formed of the composition $\{Me_2NH_2\}_4H_2V_{10}O_{28}\cdot2(CH_3)_2NCHO$, whose structure was proved by X-ray diffraction (XRD) analysis.

The decavanadate anion is of elliptic form (see the figure) and is located in a special position in the inversion center. The vanadium atoms have a distorted octahedral geometry. The measured lengths of V–O bonds with the oxygen located inside the vanadate anion vary in the range 2.25–2.35 Å, the length of conditionally ordinary V–O bond with external oxygen atoms varies in the range 1.85–1.95 Å. The length of conditionally double bonds V–O with the terminal oxygen atoms is on the average 1.6 Å. These values are in good agreement with the data obtained earlier for the vanadate anions [10–12, 23, 24]. Overcoming the difficulties in localizing protons on the background of metal oxide system we found the positions of protons on the peaks of the electron density of the anion in good agreement with the observed asymmetry of lengths of V–O bonds and the formation of intermolecular hydrogen bonds between the vanadate anions in the crystal. In total the intermolecular hydrogen bonds play a key part in the crystal packing providing the connection between the vanadate anions, dimethylammonium cations, and DMF molecules whose carbonyl groups are also involved in the intermolecular hydrogen bonds.

As shows the complex composition, in the course of the cluster formation a hydrolysis of DMF occurs simultaneously resulting in dimethylammonium cations. This is a special feature of this process since the preparation of the cluster in the form of ammonium salt required previously a direct use of amines or ammonium salts [13–17, 23, 24]. Besides an oxidation of vanadium(IV) occurred, and it was also nontrivial, for the formation of vanadium(IV) complexes from vanadyl(IV) acetylacetonate was known to proceed without changes in the oxidation state [25]. This is simultaneously an advantage of this procedure of the cluster preparation since earlier it was necessary to use less accessible vanadyl(V) acetylacetonate [23], or inorganic salts of vanadium acid [11, 12].

In the absence of 2-hydroxy-2-trifluoromethylchroman-4-one we failed to obtain the cluster both in analogous conditions and at reflux. We attempted to establish the influence of the structure and strength of Brønsted acids (Scheme 1) present in the reaction mixture on the possibility of the formation of the decavanadate cluster, and we found that only in the presence of the proper 2-hydroxy-2-trifluoromethyl-chroman-4-one or its synthetic precursor, 2'-hydroxy-acetophenone, the formation occurred of tetradimethyl-ammonium dihydrodecavanadate(V). In the other explored cases the reaction mixture either suffered tarring or crystals separated of the initial $VO(acac)_2$. The observed relation is apparently due to the chelating ability of 2'-hydroxyacetophenone and its derivatives in contrast to all other used Brønsted acids.

Scheme 2.



The catalytic activity of decavanadate cluster is known for the oxidation of hydrogen sulfide [19], starch [20], glutamic acid [26], for ethylene oxide oligomerization [21], and dehydrogenation of alkanes and alcohols [10]. In this study we investigated the catalytic activity of tetradimethylammonium dihydrodecavanadate(V) in toluene and *o*-xylene oxidation (Scheme 2).

The reactions were performed by boiling alkylbenzenes in the presence of 0.5 mol % of decavanadate cluster which did not dissolve throughout the whole process. On the completion of the reaction the precipitate was filtered off, the composition and the structure of the oxidation products was analyzed by GC-MS method. The obtained data show that the decavanadate cluster provides a possibility to oxidize the methyl groups of toluene and *o*-xylene prevailingly to an aldehyde group. Toluene conversion in 18 h was 2%, that of *o*-xylene, 6%. In the latter case the main reaction product was *o*-methylbenzaldehyde (64%), and *o*-methylbenzoic acid (3.7%) and *o*-methylbenzyl alcohol (3.5%) were also present. Thus the decavanadate cluster is a promising catalyst of alkylbenzenes oxidation.

EXPERIMENTAL

XRD experiment was performed on an automatic diffractometer Xcalibur S equipped with a CCD-detector along a standard procedure [MoK_α-radiation, graphite monochromator, ω-scanning with a step 1° at 120(2) K] on an orange prismatic crystal of the size 0.26 × 0.14 × 0.05 mm. Analytical correction for extinction was introduced. Crystal triclinic, space group *P*-1, *a* 9.5593(11), *b* 10.3690(12), *c* 10.5341(11) Å, α 95.291(9)°, β 101.697(9)°, γ 95.244(10)°, *V* 1011.6(2) Å^3. $C_{14}H_{48}N_6O_{30}V_{10}$, *Z* 1, *M* 1289.98, ρ_{calc} 2.118 g/cm^3, μ 2.302 mm^{-1}. At scattering angles 2.63° > θ > 33.55° 10990 reflections were collected, 6870 among them were independent (R_{int} 0.0246), among them 3775 with $I > 2\sigma(I)$. Completeness within the angles θ < 26.0° was 98.6%.The structure was solved and refined with the use of SHELXTL software [27] in anisotropic approximation for nonhydrogen atoms. Hydrogen atoms of C–H bonds and of a part of NH groups were placed in calculated positions and were included in the refinement in the *rider* model, the positions of the other protons were refined independently in an isotropic approximation. The final refinement results are as follows: R_1 0.0674, wR_2 0.0664 (for all reflections), R_1 0.0332, wR_2 0.0645 [for reflections with $I > 2\sigma(I)$], *GooF* 1.002. The peaks of residual electron density are 1.220/–0.549 ēÅ^{-3}. The XRD results are deposited in the Cambridge Crystallographic Data Centre, CCDC 1574175. The data are free to obtain at the address: www.ccdc.cam.ac.uk.

To estimate the catalytic activity of tetradimethylammonium dihydrodecavanadate(V) toluene and *o*-xylene were boiled under reflux in the presence of 0.5 mol % of the cluster. On the completion of the reaction the precipitate was filtered off, the filtrate was analyzed on a GC-MS instrument Agilent GC 7890A MS 5975C Inert XL EI/CI equipped with a quadrupole mass spectrometer detector (GC-MSD) and a quartz capillary column HP-5MS 30 m × 0.25 mm, film thickness 0.25 μm (polydimethylsiloxane, 5% of grafted phenyl groups). Oven temperature 40°C (3 min), heating at the rate 10°C/min till 290°C (30 min), temperature of vaporizer 250°C, of ion source 230°C, of quadrupole 150°C, of transition chamber 280°C. Carrier gas helium, split ratio 1 : 50, flow through the column 1.0 mL/min. Chromatograms were registered at scanning for total ionic current in the mass range 20–1000 Da in EI mode (70 eV).

Decavanadate cluster. In 20 mL of DMF 0.53 g (2 mmol) of $VO(acac)_2$ and 0.46 g (2 mmol) 2-hydroxy-2-trifluoromethylchroman-4-one or 0.24 mL (2 mmol) of 2'-hydroxyacetophenone was dissolved, the mixture was boiled for 2 h, then the solution was left standing till evaporation of DMF. After 2 days orange crystals were formed. Yield 0.15 g (60%). Found, %: C 12.89; H 3.94; N 6.45; V 39.22. $\{Me_2NH_2\}_4H_2V_{10}O_{28}\cdot 2(CH_3)_2NCHO$. Calculated, %: C 13.02; H 3.78; N 6.51; V 39.53.

2-Hydroxy-2-trifluoromethylchroman-4-one was obtained by procedure [28]. The other reagents (Alfa Aesar) were used without further purifications.

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