C–H Activation

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Generation, Reactivity Towards Hydrocarbons, and Electronic Structure of Heteronuclear Vanadium Phosphorous Oxygen Cluster Ions**

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Dedicated to Professor Giulia de Petris

Ranging from catalytic processes in biology, such as those catalyzed by the P-450 enzymes,[1] to heterogeneous or homogeneous catalysts used in large scale conversions,[2] oxygen-based systems represent a hallmark in contemporary catalysis and continue to attract interest.[3] One approach to address this timely topic takes advantage of the effective interplay of mass spectrometric experiments with computational methods, which allow further insight into the intrinsic properties of these oxygen-containing compounds.[4]

A key issue in this context concerns the oxygen-induced homolytic C–H bond scission of saturated and unsaturated hydrocarbons. For example, hydrogen-atom abstraction from CH_4 to generate $CH_3^{\bullet}$ is viewed as the decisive step in the oxidative dehydrogenation and dimerization of methane.[5] While the nature of the active metal-oxide surface species is still under debate in heterogeneous catalysis,[6] the crucial role of oxygen-centered radicals to bring about hydrogen abstraction by metal oxides according to reaction (1) has been

$$MO^{\bullet} + CH_4 \rightarrow CH_3^{\bullet} + MOH \qquad (1)$$

suggested in many studies,[7] including well-defined gas-phase experiments with the metal oxides $[MgO]^{\bullet+}$,[8] $[FeO]^{\bullet+}$,[9] $[PbO]^{\bullet+}$,[10] $[MoO_3]^{\bullet+}$,[11] $[ReO_3(OH)]^{\bullet+}$,[12] $[OsO_4]^{\bullet+}$,[13] $[V_4O_{10}]^{\bullet+}$,[14] and $[(Al_2O_3)_x]^{\bullet+}$ ($x = 3$–5),[15] as well as the metal-free oxides $[SO_2]^{\bullet+}$ and $[P_4O_{10}]^{\bullet+}$.[16,17] The latter one represents the first gaseous polynuclear metal-free cluster that is capable of hydrogen-atom abstraction from methane at ambient conditions; thus, it deemed of interest to compare its properties with the isostructural transition-metal cluster $[V_4O_{10}]^{\bullet+}$, which had been suggested earlier to serve as an appropriate model for surface-mediated C–H bond activation processes.[18] These two structural analogues show a comparable behavior in the reaction with methane; however, the reactivity patterns with ethane and ethylene differ dramatically. While $[P_4O_{10}]^{\bullet+}$ reacts with both substrates predominantly by homolytic C–H bond cleavage, $[V_4O_{10}]^{\bullet+}$ only gives rise to the oxygen-atom transfer to the hydrocarbons.[19] Therefore, studying the effects caused by the systematic variation of the vanadium/phosphorous ratios, that is generating and probing the reactivity of the cationic clusters $[V_3PO_{10}]^{\bullet+}$, $[V_2P_2O_{10}]^{\bullet+}$, and $[VP_3O_{10}]^{\bullet+}$ is an appropriate approach. In addition, the enormous interest in these systems also derives from their close relations to the so-called vanadium phosphorus oxide (VPO) catalysts, which are used for highly selective oxidation and bond activation processes.[20] Finally, there is the question about the nature of the active site in mixed oxo-clusters. For example, for $[AlVO_4]^{\bullet+}$ it is exclusively the radical site that is located at the terminal Al=O group which is responsible for C–H bond scission of methane at room temperature.[21]

Herein we present our results on the mixed metal/nonmetal oxide cluster ions $[V_nP_{4-n}O_{10}]^{\bullet+}$ ($n = 1$–3) and describe their generation, reactivity towards small hydrocarbons, and electronic and structural properties. By using a relative simple preparation, the precursor $VOPO_4{\cdot}2H_2O$ can easily be synthesized, subsequently dried, and finally sintered to prepare small targets suitable for the laser-vaporization/ionization source of an FT-ICR mass spectrometer (Figure 1). By this procedure, two of the three clusters of interest, that is $[V_3PO_{10}]^{\bullet+}$ and $[V_2P_2O_{10}]^{\bullet+}$, can be generated in the gas phase (for more details about the target preparation and the instrumental setup, see the Experimental Section). Despite the numerous efforts in the modification of the target and in

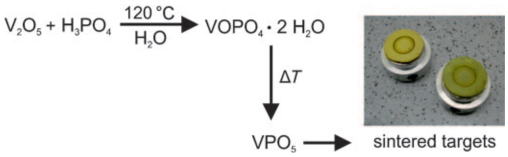

Figure 1. Preparation and picture of suitable targets for the laser-induced generation of $[V_2P_2O_{10}]^{\bullet+}$ and $[V_3PO_{10}]^{\bullet+}$.

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the optimization of the experimental parameters of the mass spectrometer, the $[VP_3O_{10}]^{\bullet+}$ cluster could not be generated, possibly as a result of the unfavorably high ionization energies of the respective VP_3O_{10} cluster.[22]

The mixed cluster ions $[V_2P_2O_{10}]^{\bullet+}$ and $[V_3PO_{10}]^{\bullet+}$ were generated in sufficient yields, mass selected, and exposed to methane in the reaction cell at stationary pressures in the order of 2×10^{-8} mbar. As shown in Figure 2, both clusters bring about efficient homolytic C−H bond cleavage of methane at room temperature, according to Equations (2) and (3).

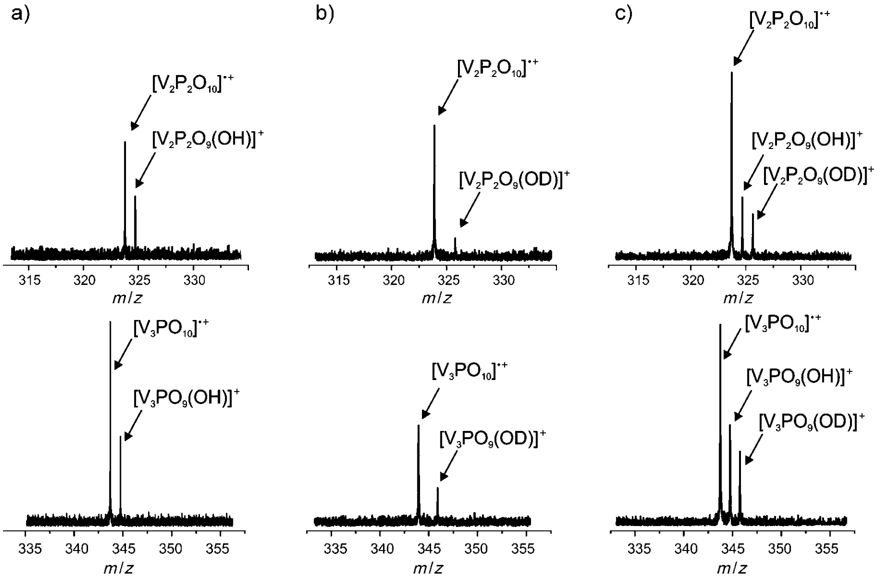


Figure 2. Mass spectra showing the reactivity of $[V_2P_2O_{10}]^{\bullet+}$ and $[V_3PO_{10}]^{\bullet+}$ with methane at 2.1×10^{-8} mbar: a) CH_4, b) CD_4, and c) CH_2D_2.

$$[V_2P_2O_{10}]^{\bullet+} + CH_4 \rightarrow [V_2P_2O_9(OH)]^+ + CH_3^{\bullet} \qquad (2)$$

$$[V_3PO_{10}]^{\bullet+} + CH_4 \rightarrow [V_3PO_9(OH)]^+ + CH_3^{\bullet} \qquad (3)$$

From the kinetic analysis, the rate constants of $k([V_2P_2O_{10}]^{\bullet+}) = 5.6\times10^{-10}\,cm^3\,s^{-1}$ molecule^{-1} and $k([V_3PO_{10}]^{\bullet+}) = 5.2\times10^{-10}\,cm^3\,s^{-1}$ molecule^{-1} were derived; these correspond to reaction efficiencies of 57% and 53%, relative to the collision rate. These efficiencies are on the same order of magnitude as for the previously reported pure cluster ions $[V_4O_{10}]^{\bullet+}$ and $[P_4O_{10}]^{\bullet+}$; further, the intramolecular kinetic isotope effects (KIEs), derived from the $[V_2P_2O_{10}]^{\bullet+}/CH_2D_2$ and $[V_3PO_{10}]^{\bullet+}/CH_2D_2$ couples, are in excellent agreement with earlier findings, thus amounting to KIE = 1.3 ± 0.1 for $[V_2P_2O_{10}]^{\bullet+}$ and to KIE = 1.2 ± 0.1 for $[V_3PO_{10}]^{\bullet+}$.[23]

Further insight into the electronic structure of the clusters and the mechanistic details about their reactions with methane is provided by density functional calculations. According to UB3LYP computations, the most stable isomer of all five clusters $[V_nP_{4-n}O_{10}]^{\bullet+}$ (n = 0–4) corresponds to a slightly distorted tetrahedral cage structure, with one terminal X=O bond (X = V, P) that is significantly elongated (compared to the neutral cluster) as a result of the removal of an electron from the double bond (Figure 3). The most notable feature of all-mixed clusters $[VP_3O_{10}]^{\bullet+}$, $[V_2P_2O_{10}]^{\bullet+}$, and $[V_3PO_{10}]^{\bullet+}$ concerns the distribution of the spin density (indicated by the blue isosurface in Figure 3).

For the corresponding neutral clusters, orbital analysis showed that the HOMO in all these vanadium/phosphorous-containing clusters corresponds to the π-bonding orbital of the terminal P=O bond; thus, removing an electron from this orbital in the laser-ionization process results in phosphorous-bound oxygen-centered radicals as the most stable isomers, respectively. An isomeric cluster with the spin located at the vanadium-bound oxygen atom V−O$^{\bullet}$ could only be located as a local minimum on the potential energy surface (PES) in the case of $[V_3PO_{10}]^{\bullet+}$ with a relative energy of 74 kJ mol^{-1} compared to the P−O$^{\bullet}$ isomer.[24] Thus, homolytic C−H bond scission takes place solely at the phosphorous-bound oxygen atom.

Not entirely unexpectedly, the PESs of $[V_3PO_{10}]^{\bullet+}$ and $[V_2P_2O_{10}]^{\bullet+}$ in their reactions with methane (Figure 4) resemble strongly the reaction mechanisms reported earlier for $[P_4O_{10}]^{\bullet+}$ and $[V_4O_{10}]^{\bullet+}$.[14,17] Smooth, barrier-free hydrogen-atom abstraction from methane to the cluster leads to an intermediate in which the methyl group is only loosely coordinated to the hydrogen atom of the newly formed phosphorous-bound hydroxy group. For both systems, the formation of this intermediate is associated with a significant energy gain of −137 kJ mol^{-1} for $[V_2P_2O_9(OH)/CH_3]^{\bullet+}$ and −127 kJ mol^{-1}

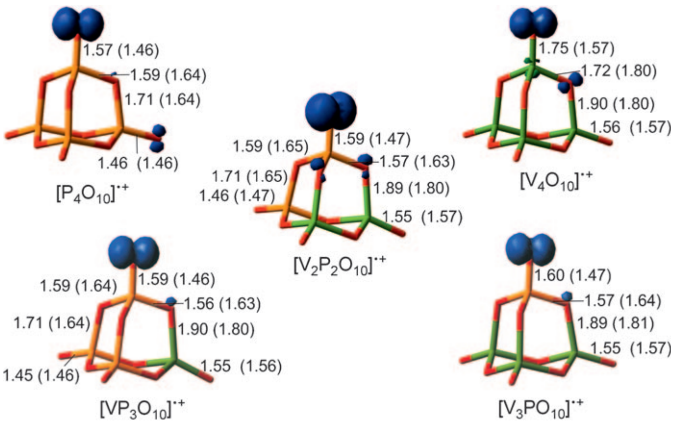


Figure 3. Lowest-energy structures calculated for $[V_nP_{4-n}O_{10}]^{\bullet+}$ (n = 0–4) (V green, P yellow, O red). The blue isosurface indicates the spin density within the respective cluster. Bond lengths for the cationic and the according neutral cluster (in parentheses) are given in Å.

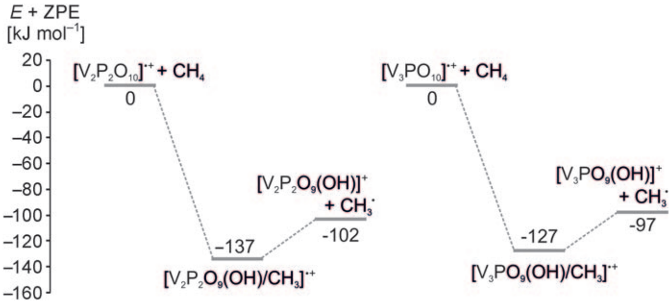


Figure 4. Energy diagram for the reaction of $[V_2P_2O_{10}]^{\bullet+}$ (left) and $[V_3PO_{10}]^{\bullet+}$ (right) with methane. The values derived by DFT are given relative to the respective entrance channel and are corrected for zero-point energies.

for $[V_3PO_9(OH)/CH_3]^{\bullet+}$. The reactions are completed by the liberation of the methyl radical $CH_3^{\bullet}$ concomitant with the formation of $[V_2P_2O_9(OH)]^+$ and $[V_3PO_9(OH)]^+$, respectively; the computed exothermicities amount to $-102\ kJ\,mol^{-1}$ for $[V_2P_2O_9(OH)]^+$ and to $-97\ kJ\,mol^{-1}$ for $[V_3PO_9(OH)]^+$.

This combined experimental and computational study is, to our knowledge, the first example for a successful generation and investigation of mixed vanadium phosphorous oxide clusters in the gas phase. In addition to their reactivity towards methane, these systems may help to further probe the interaction between metals and/or non-metals as well as the role of vanadium in oxo-frameworks. Thus, the generation of these clusters provides an opportunity to explore the reactivity of these mixed VPO-systems towards larger hydrocarbons, for which the reactivity patterns of $[P_4O_{10}]^{\bullet+}$ and $[V_4O_{10}]^{\bullet+}$ differ dramatically.[14,17,19] Quite unexpectedly, the reactions of $[V_3PO_{10}]^{\bullet+}$ and $[V_2P_2O_{10}]^{\bullet+}$ with ethane and ethylene give rise to completely new product distributions, as shown in Figure 5, for the couples $[V_3PO_{10}]^{\bullet+}/C_2H_x$ and $[V_2P_2O_{10}]^{\bullet+}/C_2H_x$ ($x=4$, 6). While homolytic C–H bond scission, according to Equations (4a) and (5a), occurs, oxygen-atom transfer does not take place [Eqs. (4b) and (5b)]. The occurrence of the reaction shown in Equations (4a) and (5a) and the lack of an oxygen-atom transfer suggests once more that the radical site must be located at the phosphorous-bound oxygen atom, based on the distinctly different reactivity pattern of $[P_4O_{10}]^{\bullet+}$ versus $[V_4O_{10}]^{\bullet+}$. More surprisingly, as a new reaction channel double C–H bond activation, that is dehydrogenation of ethane and ethylene, according to Equations (4c) and (5c) takes place; this reaction has not been observed in the reactions of C_2H_x ($x=4$, 6) with $[P_4O_{10}]^{\bullet+}$ and $[V_4O_{10}]^{\bullet+}$, respectively. Based on the reactions with CH_3CD_3 and CH_2CD_2, double hydrogen (deuterium) transfer proceeds in a clean [1,2]-fashion which is not proceeded by H/D scrambling. The rate constants, efficiencies and KIEs for each reaction, derived from kinetic analysis, are given in Table 1. Compared to the reaction with methane, the larger rate constants and the increased efficiency are in excellent agree-

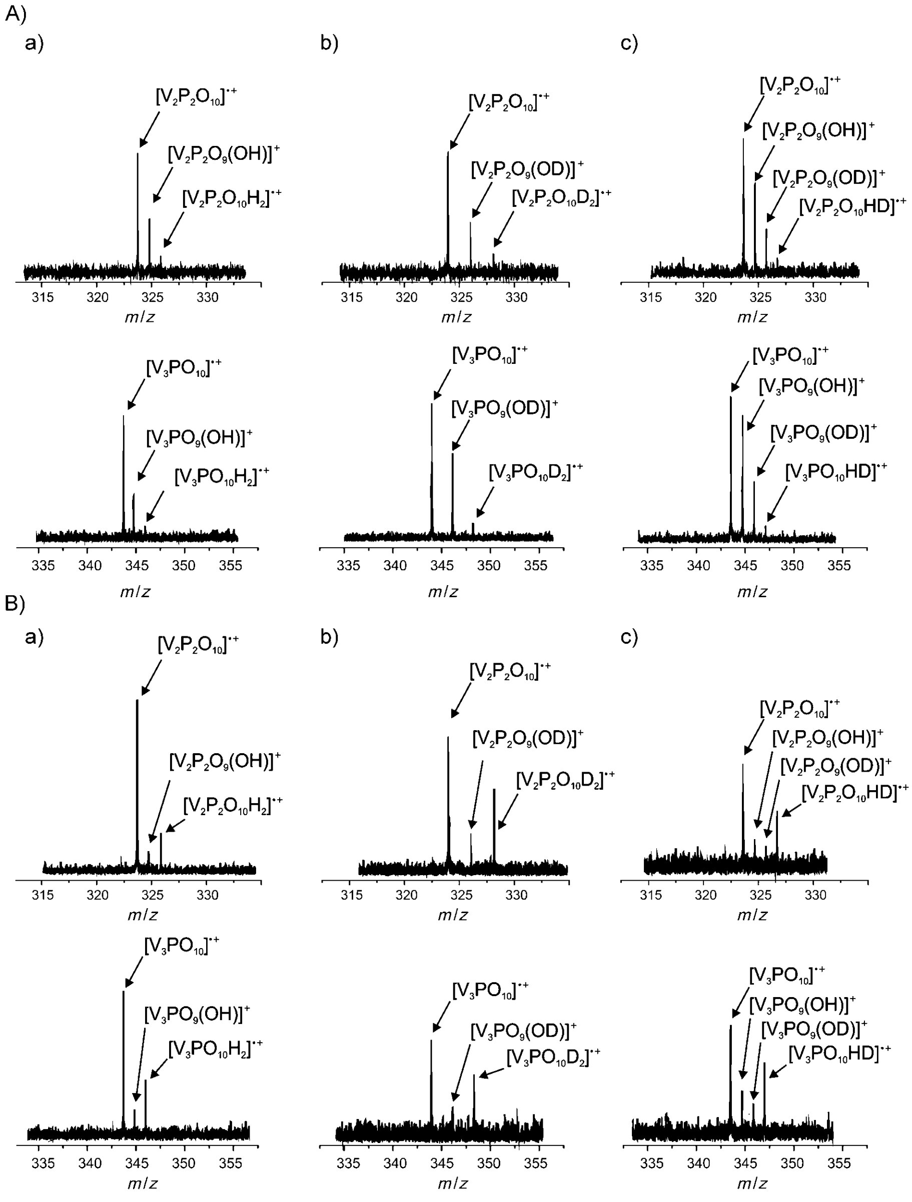
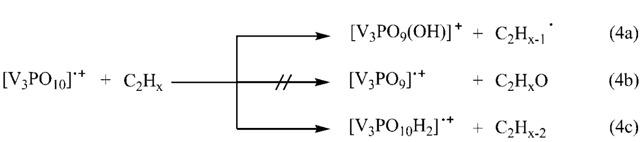


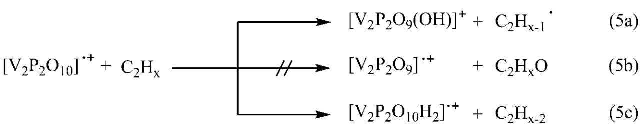
Figure 5. Mass spectra showing the reactivity of $[V_2P_2O_{10}]^{\bullet+}$ and $[V_3PO_{10}]^{\bullet+}$ with A) ethane [a) C_2H_6, b) C_2D_6, c) CH_3CD_3] and B) ethylene at 2.2×10^{-8} mbar [a) C_2H_4, b) C_2D_4, c) CH_2CD_2].

Table 1: Absolute rate constants *k* (given in $\times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$), reaction efficiencies ϕ (given in %, relative to the collision rate), and intramolecular KIEs (for the homolytic C–H bond scission) in the respective reaction couples $[V_nP_{4-n}O_{10}]^{\cdot+}/C_2H_x$ ($n=2, 3$; $x=4, 6$).

	$[V_3PO_{10}]^{\cdot+}$/ C_2H_6	$[V_2P_2O_{10}]^{\cdot+}$/ C_2H_6	$[V_3PO_{10}]^{\cdot+}$/ C_2H_4	$[V_2P_2O_{10}]^{\cdot+}$/ C_2H_4
k	8.7	5.9	7.1	5.5
ϕ	93	62	76	58
KIE	1.9	2.2	1.4	1.3

ment with the previously reported findings on $[P_4O_{10}]^{\cdot+}$ and $[V_4O_{10}]^{\cdot+}$. The larger KIEs may suggest a mechanistically more complex homolytic C–H bond activation step instead of a direct hydrogen-atom abstraction.[25]





So far, only few small mono- or dinuclear metal oxide cations are known to show this kind of reactivity towards C_2-hydrocarbons; for example, $[VO_2]^+$ [26] and $[SO_2]^{\cdot+}$ [27] bring about double C–H bond activation of ethane at room temperature, while $[ReO_3]^+$ [12] and $[Fe_2O_2]^{\cdot+}$ [28] dehydrogenate ethylene under these mild conditions. Unfortunately, the suggested reaction mechanisms for these systems cannot be simply adopted for these larger VPO systems and preliminary computations point to a rather complex potential-energy surface which needs to be treated separately.

Clearly, while more sophisticated computational studies are warranted to provide a quantitative picture, the present work emphasizes once more the critical role of cluster ion compositions in C–H bond-activation processes.[29]

Experimental Section

The inorganic precursor $VOPO_4 \cdot 2H_2O$ was prepared by a slightly modified procedure,[30] whereby V_2O_5 (24 g, 132 mmol) was heated at reflux (120 °C) in a suspension of distilled water (550 mL) and concentrated H_3PO_4 (150 mL) for 24 h. A green-yellow, crystalline solid was isolated by vacuum filtration. The product was washed sparingly with water, ethanol, and then acetone and dried for several days under high vacuum at room temperature. $VOPO_4 \cdot 2H_2O$ (42 g, 211 mmol, 80 %) was recovered as a yellow powder and identified by X-ray powder diffraction (Siemens D 5000 diffractometer, $Cu_{K\alpha 1}$ radiation, Bragg–Brentano geometry). The exact water content of the $VOPO_4 x H_2O$ phase was determined to $x = 1.95$ by thermogravimetric analysis (NETZSCH STA 409). Additional thermoanalytical measurements in air point to complete water loss at about 150 °C and melting of the resulting powder at about 800 °C. The powder, which can be described as poorly crystalline vanadyl phosphate, was pressed to pellets (diameter: 12 mm, thickness 1–1.5 mm) and sintered in air for 24 h at 700–750 °C in a conventional chamber furnace. The mechanical stability of the resulting pellets is sufficient for the procedures described below.

The reactivity experiments were performed on a modified Bruker/Spectrospin CMS47X mass spectrometer, equipped with an Apex III data station and a 4.7 T superconducting magnet. The vanadium phosphorous oxygen cluster cations were produced by laser vaporization[31] of a rotating VPO-target with a 5 ns laser pulse of a frequency-doubled Nd:YAG laser (Continuum Surelite II, 10 Hz, 5 mJ pulse energy), followed by supersonic expansion of the hot plasma in a triggered helium pulse. The transport of the produced VPO-clusters was accomplished by an electrostatic lens system through differential pumping stages into the ultrahigh vacuum region, where the ions have been mass-selected and stored in the ICR cell. The reactivity was studied by introducing the hydrocarbons methane, ethane and ethylene by a needle leak valve at stationary pressures on the order of 2×10^{-8} mbar. The experimental second-order rate constants are evaluated assuming pseudo first-order kinetic approximation after calibration of the measured pressures and acknowledgment of the ion gauge sensitivities;[32] the error of the absolute rate constants is assumed to be ±30 %.

All calculations were performed using the hybrid density functional theory method UB3LYP[33] with triple-ζ plus polarization basis sets TZVP.[34] Vibrational frequency analyses were performed at the same level of theory to characterize the nature of stationary points as minima or transition structures, and to derive the zero-point energy (all energetic values given in this work are corrected for zero-point energy). The Gaussian03 program suite was used for the calculations.[35]

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[23] The respective values for $[V_4O_{10}]^{\bullet +}$ and $[P_4O_{10}]^{\bullet +}$, taken from the References [14] and [17], are $k([V_4O_{10}]^{\bullet +}) = 5.5\times10^{--10}$ cm^{3}s^{-1} and $k([P_4O_{10}]^{\bullet +}) = 6.4\times10^{--10}$ cm^{3}s^{-1}; KIE($[V_4O_{10}]^{\bullet +}$) = 1.3 and KIE($[P_4O_{10}]^{\bullet +}$) = 1.6.

[24] Owing to the rather small or even non-existing barriers, structure optimization were in the case of $[V_2P_2O_{10}]^{\bullet +}$ and $[VP_3O_{10}]^{\bullet +}$ only possible by fixing the terminal V=O bond to 1.75 Å, as reported for the structure of $[V_4O_{10}]^{\bullet +}$. The resulting relative energies for isomers with V-O$^\bullet$ units are 92 kJ mol^{-1} for $[V_2P_2O_{10}]^{\bullet +}$ and 71 kJ mol^{-1} for $[VP_3O_{10}]^{\bullet +}$, respectively.

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