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Competitive Hydrogen-Atom Abstraction versus Oxygen-Atom and Electron Transfers in Gas-Phase Reactions of $[X_4O_{10}]^{\bullet +}$ (X = P, V) with C_2H_4

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In memoriam Professor Herbert Schumann

Despite enormous efforts and considerable research activities conducted over the past decades, oxidative coupling of methane (OCM) remains a challenge for contemporary catalysis.[1] In the context of catalytic C–H bond activation of saturated and unsaturated hydrocarbons, as being realized in large-scale chemical processes, a detailed mechanistic description of the elementary processes and a complete understanding of the functional and structural properties of the reactive sites of, for example, solid-state catalysts are still limited.[2]

Over the last few years the investigation of small cluster systems, in particular metal and metal oxide species, using advanced mass-spectrometric methods in conjunction with theoretical studies proved useful in elucidating mechanistic aspects.[3] Based on these and other studies there is now consensus that in the context of C–H bond activation the enhanced reactivity of metal-oxide based catalysts is due to the presence of oxygen-centered radicals.[4] In the case of OCM, these oxygen-centered radicals bring about efficient hydrogen-atom abstraction from CH_4 to generate $CH_3^{\bullet}$, and this step is considered to be decisive for the oxidative dehydrogenation and dimerization of methane.[1,5] Hydrogen-atom abstraction has also been observed in well-defined gas-phase experiments, and various mechanistic variants were unraveled in combination with quantum-chemical calculations. In fact, numerous examples for the effective room-temperature activation of methane by a structurally rather diverse set of metal oxides have been studied, including $[MgO]^{\bullet +}$,[6] $[FeO]^{\bullet +}$,[7] $[MoO_3]^{\bullet +}$,[8] $[ReO_3(OH)]^{\bullet +}$,[9] $[OsO_4]^{\bullet +}$,[10] $[V_4O_{10}]^{\bullet +}$,[11] and $[(Al_2O_3)_x]^{\bullet +}$ ($x = 3, 4, 5$),[12] as well as the recently reported metal-free oxides $[SO_2]^{\bullet +}$ and the polynuclear oxide cluster $[P_4O_{10}]^{\bullet +}$.[13,14] The latter brings about H-atom transfer at 298 K with a rate constant of $k = 6.4 \times 10^{-10}\,cm^3\,s^{-1}\,molecule^{-1}$ [Eq. (1)].[14]

$$[P_4O_{10}]^{\bullet +} + CH_4 \rightarrow [P_4O_9(OH)]^{+} + CH_3^{\bullet} \quad (1)$$

Not entirely unexpected and in line with observations with other gas-phase bond-activation processes,[15] the chemoseletivity of these reactions varies considerably for different couples of oxide ions and hydrocarbon substrates. For example, Castleman and co-workers observed in the reaction of $[V_4O_{10}]^{\bullet +}$ with C_2H_n ($n = 4, 6$) the oxidation of the hydrocarbons due to oxygen-atom transfer [Eq. (2)].[16]

$$[V_4O_{10}]^{\bullet +} + C_2H_n \rightarrow [V_4O_9]^{\bullet +} + C_2H_nO \quad (2)$$

As to the chemical nature of the oxygenated products, according to DFT calculations, C_2H_4 gives rise to the formation of acetaldehyde (CH_3CHO) rather than ethylene oxide in the O-atom transfer; thus, hydrogen migration is involved in the reaction.[17] Similar results have been reported for the polynuclear clusters $[V_2O_5]^{\bullet +}$,[17] $[Ag_2O]^{\bullet +}$,[18] $[Zr_2O_4]^{\bullet +}$ and $[Zr_4O_8]^{\bullet +}$,[19] as well as for the anionic cluster $[Zr_2O_5]^{\bullet -}$.[20,21]

For the isostructural tetranuclear phosphorus oxide cluster $[P_4O_{10}]^{\bullet +}$,[11,14] O-atom transfer to C_2H_6 does not take place; rather, hydrogen-atom abstraction dominates, thus producing the cationic closed-shell species $[P_4O_9(OH)]^{+}$ [Eq. (3)].[22]

$$[P_4O_{10}]^{\bullet +} + C_2H_6 \rightarrow [P_4O_9(OH)]^{+} + C_2H_5^{\bullet} \quad (3)$$

Here we describe the gas-phase reaction of $[P_4O_{10}]^{\bullet +}$ with C_2H_4, and the findings reveal an unexpected reactivity in comparison with the well-studied $[V_4O_{10}]^{\bullet +}/C_2H_4$ system.[16,17] For example, the $[P_4O_{10}]^{\bullet +}/C_2H_4$ couple does not react by oxygen-atom transfer to the unsaturated hydrocar-

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bon [Eq. (4)]. Rather, two different reaction channels occur at room temperature, one corresponds to hydrogen-atom abstraction [Eq. (5)] and the other to a single-electron transfer (SET) according to Equation (6), respectively, with a branching ratio of approximately 1:1 (see Figure 1).[23]

$$[P_4O_{10}]^{\bullet +} + C_2H_4 \not\rightarrow [P_4O_9]^{\bullet +} + C_2H_4O \tag{4}$$

$$[P_4O_{10}]^{\bullet +} + C_2H_4 \rightarrow [P_4O_9(OH)]^{+} + C_2H_3^{\bullet} \tag{5}$$

$$[P_4O_{10}]^{\bullet +} + C_2H_4 \rightarrow P_4O_{10} + [C_2H_4]^{\bullet +} \tag{6}$$

From a kinetic analysis, a rate constant of $k = 2\times 10^{-9}\,cm^3\,s^{-1}\,molecule^{-1}$ was derived, corresponding to an efficiency of 100% in terms of collision rate. By the use of C_2D_4 and CH_2CD_2 (Figure 1b, c) no significant kinetic isotope effect (KIE = 1.05) was found for the homolytic C–H(D) bond cleavage. The formation of the closed-shell ion $[C_3H_5]^+$ can be traced back to an efficient secondary reaction of $[C_2H_4]^{\bullet +}$ with another neutral molecule of ethene [Eq. (7)], resulting in the formation of an allyl cation, as studied in detail quite some time ago.[24] The rate constant $k = 0.85\times 10^{-9}\,cm^3\,s^{-1}\,molecule^{-1}$ for this secondary reaction is in the same order of magnitude as the primary reaction.[24d]

$$[C_2H_4]^{\bullet +} + C_2H_4 \rightarrow [C_3H_5]^{+} + CH_3^{\bullet} \tag{7}$$

Insight into the mechanistic details of the homolytic C–H bond activation step of C_2H_4 by $[P_4O_{10}]^{\bullet +}$ is provided by density functional theory (DFT) calculations. According to UB3LYP-based computations, the coordination of ethene to the lowest-energy structure of $[P_4O_{10}]^{\bullet +}$, which corresponds to a slightly distorted tetrahedral cage structure with C_S symmetry, possessing an oxygen-centered radical at one of the terminal phosphoryl oxygen atom,[14] results in a smooth, barrier-free hydrogen-atom abstraction process, associated with an energy gain of 176 kJ mol^{-1} (Figure 2). In the intermediate complex, the C_2H_3 fragment is rather loosely coordinated to the hydrogen atom of the newly formed, phosphorus-bound hydroxy group; the reaction is completed by ejection of a $C_2H_3^{\bullet}$ radical concomitant with formation of $[P_4O_9(OH)]^+$. The computed exothermicity amounts to 109 kJ mol^{-1}. This mode of a *direct* abstraction process, in contrast to a metal-mediated *indirect* one as suggested for the $[MgO]^{\bullet +}/CH_4$ couple,[6] seems to be rather general as it

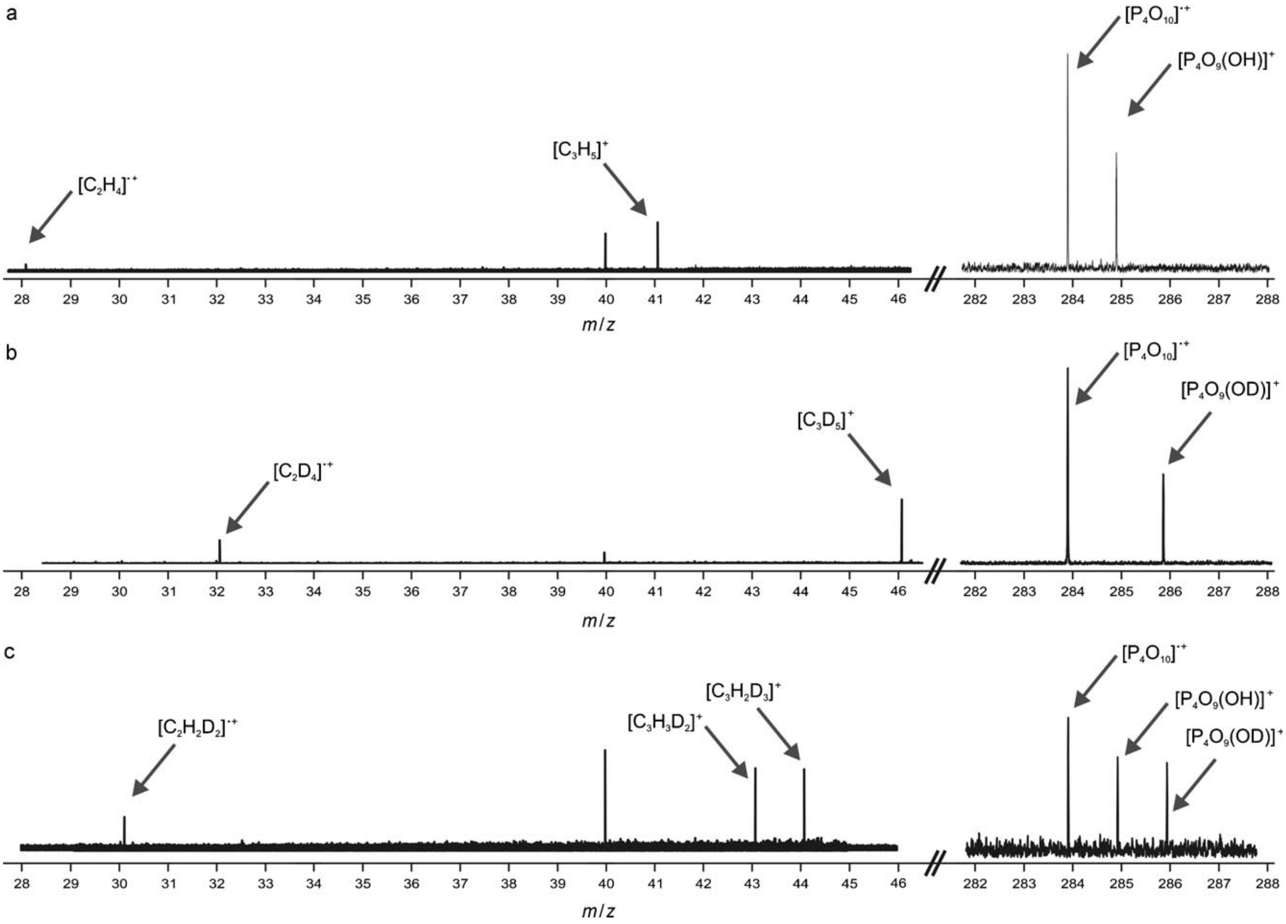

Figure 1. Mass spectra showing the reactivity of $[P_4O_{10}]^{\bullet +}$ with ethene at 2.2×10^{-9} mbar: a) C_2H_4 , b) C_2D_4, and c) CH_2CD_2. The signal at *m/z* 39.97 is attributed to ionized argon, which was used as pulse gas to thermalize the hot ions.

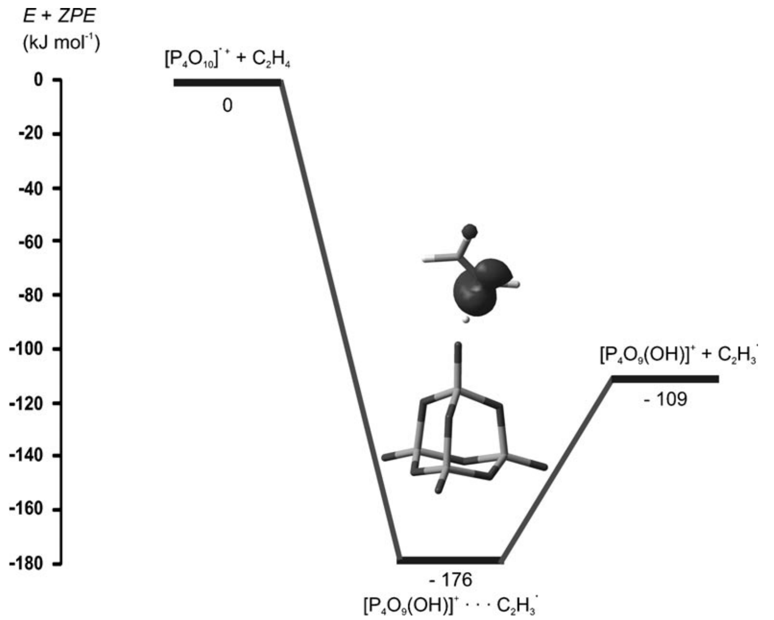

Figure 2. Energy diagram for the radical hydrogen abstraction from ethene by bare $[P_4O_{10}]^{\bullet+}$. The DFT-based values are relative to the entrance channel, corrected for zero-point energy, and given in $kJ\,mol^{-1}$. The gray surface indicates the complete spin transfer from the cluster to the hydrocarbon in the intermediate.

has been ascribed also to the reactions of $[SO_2]^{\bullet+}$ and $[P_4O_{10}]^{\bullet+}$ with CH_4[13,14] and C_2H_6[21] as well as for the $[V_4O_{10}]^{\bullet+}/CH_4$ system.[11]

Hydrogen-atom abstraction, according to [Eq. (5)], is, to the best of our knowledge, the first example of thermal activation of ethene by a polynuclear *metal-free* oxide radical cation. A comparison of $[P_4O_{10}]^{\bullet+}$ with $[V_4O_{10}]^{\bullet+}$ is also quite instructive. Even though the two cationic radical clusters have similar geometries, comparable spin densities and the same reactivity pattern in the reaction with methane, for the higher hydrocarbons, the reactivities are completely different [compare, for example, Eqs. (2)–(6)]. While a fully conclusive analysis has yet to be provided, two obvious differences concern the energetics of the oxygen-atom and electron transfers [Eqs. (2), (4), (6)]. Based on our DFT calculations the following pictures emerge: Oxygen-atom transfer according to [Eq. (8); X=P, V] is more favored by $104\,kJ\,mol^{-1}$ for X=V than for X=P; this finding reflects the significantly higher oxygen-atom affinity of $[P_4O_9]^{\bullet+}$ and explains the non-occurrence of O-transfer for $[P_4O_{10}]^{\bullet+}$ [Eq. (4)] in contrast to $[V_4O_{10}]^{\bullet+}$ [Eq. (2)].[17]

$$[X_4O_{10}]^{\bullet+} + C_2H_4 \rightarrow [X_4O_9]^{\bullet+} + C_2H_4O \qquad (8)$$

As to the single-electron transfer, the DFT calculated ionization energy (*IE*) of P_4O_{10} amounts to $1179\,kJ\,mol^{-1}$ and that of V_4O_{10} to only $1080\,kJ\,mol^{-1}$ compared with $IE(C_2H_4) = 993\,kJ\,mol^{-1}$.[25] Whereas for the $[P_4O_{10}]^{\bullet+}/C_2H_4$ couple SET takes place [Eq. (6) and Figure 1], it has not been observed for the related $[V_4O_{10}]^{\bullet+}/C_2H_4$ system at room temperature,[16] which may be a consequence of the substantial difference of the recombination energies of the two cluster ions $[X_4O_{10}]^{\bullet+}$ (X=P, V).

Further insight is gained by studying the reaction of $[V_4O_{10}]^{\bullet+}$ with C_2H_4 in a QHQ tandem mass spectrometer. At lowest collision energies, that is, thermalized conditions, oxygen-atom transfer is observed exclusively as reported previously.[16] Yet, at elevated collision energies, that is, with non-thermalized, "hot" ions, SET occurs also in the couple $[V_4O_{10}]^{\bullet+}/C_2H_4$ to give rise to $[C_2H_4]^{\bullet+}$. In contrast, homolytic C–H bond activation of C_2H_4 by $[V_4O_{10}]^{\bullet+}$ does not occur even at higher collision energies (see Figure 3). These findings illustrate once more the lower ionization potential of $[V_4O_{10}]^{\bullet+}$, as well as the lower reactivity towards homolytic C–H bond activation.

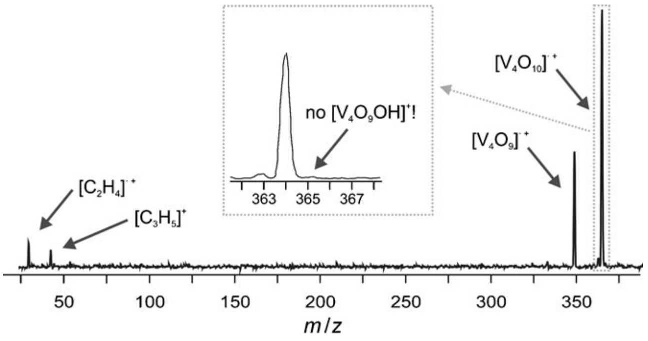

Figure 3. Mass spectra showing the reactivity of mass-selected $[V_4O_{10}]^{\bullet+}$ with ethene at 4.6×10^{-4} mbar and a collision energy of $E_{CM} = 3.0$ eV.

Clearly, while more sophisticated computational studies are warranted to provide a quantitative picture, the present work already underlines the critical role that fundamental properties, such as ionization energies or oxygen-atom affinities play in competitive gas-phase processes of cluster-oxide radical ions with simple organic substrates.[26]

Experimental and Computational Sections

The experiments with $[P_4O_{10}]^{\bullet+}$ were carried out with a Bruker APEX IV Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with a 7.05 T magnet and a standard (Bruker Bremen) 70 eV EI-source. P_4O_{10} was introduced in the EI source with a direct inlet probe at 350 °C (source temperature 180 °C). The resulting ions were trapped in the FT-ICR cell, which was operated at pressures below 10^{-10} mbar. Mass-selected $[P_4O_{10}]^{\bullet+}$ was then subjected to a pulse of argon, so that the product ions were assumed to be thermalized.[27] After careful re-isolation by single-shot excitation only and after a variable reaction pulse of 0–0.5 s, the ions were detected by a standard excitation and detection sequence. The reactivity was studied by introducing ethene by a pulse valve to create temporary pressures in the order of 2.0×10^{-9} 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[28] and corrected for pulsed introduction of the reaction gases by dividing through a scaling factor of 1.5; the error of the absolute rate constants is assumed to be ±50%.

The experiments with $[V_4O_{10}]^{\bullet+}$ were carried out using a tandem mass spectrometer with QHQ configuration (Q: quadrupole, H: hexapole) equipped with an electrospray ionization (ESI) source as described elsewhere.[29] Briefly, vanadium oxide clusters were generated by ESI of a solution of $V_6O_7(OCH_3)_{12}$ in CD_3OD. Then, $[V_4O_{10}]^{\bullet+}$ was mass-selected by using Q1 and then allowed to react with methane in the hexapole at pressures on the order of 10^{-4} mbar, which approximately corresponds to single-collision conditions, at varying collision energies $E_{CM}=0$–5 eV. The reaction was monitored by detection of the ionic products using Q2.

All calculations were performed by using the hybrid density functional theory method UB3LYP[30] with triple-ζ plus polarization basis sets TZVP.[31] 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 (ZPE). The Gaussian03 program suite was used for all the calculations.[32]

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