Oxygen-Centered Radicals

Room-Temperature C−H Bond Activation of Methane by Bare [P$_4$O$_{10}$]$^{•+}$**

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In memory of Fulvio Cacace

Hydrogen-atom abstraction from CH$_4$ to generate CH$_3$$^•$ is considered to be the key step in the oxidative dehydrogenation and dimerization of methane.[1] There is now a consensus, which is based on experimental and computational studies, that the enhanced oxidation reactivity of metal-based catalysts requires the presence of oxygen-centered radicals to bring about homolytic bond cleavage according to the reaction shown in Equation (1) (M: metal).[2] Perhaps the

$$CH_4 + OM \rightarrow CH_3^• + HOM \qquad (1)$$

most compelling experimental evidence for this concept has been provided by well-defined gas-phase studies[3] of mass-selected metal oxides that are in their electronic ground states and have various stoichiometries including [MgO]$^{•+}$,[4] [FeO]$^{•+}$,[5] [MoO$_3$]$^{•+}$,[6] [ReO$_3$(OH)]$^{•+}$,[7] [OsO$_4$]$^{•+}$,[8] and [V$_4$O$_{10}$]$^{•+}$,[9] as well as oligomeric clusters [(Al$_2$O$_3$)$_x$]$^{•+}$ ($x=3$–5).[10] For the latter system, aluminum oxide cluster cations that have an odd number of aluminum atoms and lack an oxygen-centered radical do not react with methane.[10,11] Further studies on the role of oxygen-centered radicals in chemical reactions showed that other substrates, such as ethylene or acetylene, can also be activated by different radical transition-metal oxide clusters, such as neutral VO$_3$$^•$.[12]

Room-temperature hydrogen-atom abstraction from methane by a metal-free radical cation oxide was reported recently by de Petris et al.[13] In this elegant experimental and computational study, it was demonstrated that [SO$_2$]$^{•+}$ brings about efficient activation of methane [Eq. (2)] with a rate

$$CH_4 + [SO_2]^{•+} \rightarrow CH_3^• + [SO_2H]^+ \qquad (2)$$
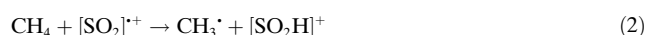
constant of $k = 6.6 \times 10^{-10}$ cm^{3}s^{-1}molecule^{-1} at 298 K; this

rate corresponds to an efficiency of 64% with respect to the collision rate. Small kinetic isotope effects (KIEs) derived from the reactions of [SO$_2$]$^{•+}$ with CD$_4$ (1.23) and CH$_2$D$_2$ (1.30) together with (CCSD(T)) calculations imply a direct abstraction process. KIEs of the same magnitude were reported earlier for the reactions of [V$_4$O$_{10}$]$^{•+}$[9] and [HO]$^•$[14] with deuterated methanes.

Herein we report our findings on the reaction of the tetranuclear phosphorous oxide cluster [P$_4$O$_{10}$]$^{•+}$ with CH$_4$. The metal-free [P$_4$O$_{10}$]$^{•+}$/CH$_4$ system exhibits many structural as well as reactivity features that are remarkably similar to those of the previously investigated tetranuclear [V$_4$O$_{10}$]$^{•+}$ cluster;[9] the latter had been suggested to serve as an appropriate model for surface-mediated C−H bond activation processes.[15] P$_4$O$_{10}$ has had only a few applications in synthetic chemistry to date, predominantly as a drying agent, but further investigations are necessary to estimate its full potential as a possible heterogeneous metal-free catalyst at ambient temperatures. In addition, the enhanced reactivity of [P$_4$O$_{10}$]$^{•+}$ may shed new light on the common assumption that the phosphates, which are used in industry as linkers between catalytically active metal oxide sites, are catalytically inactive.[2f,16]

As shown in Figure 1, mass-selected [P$_4$O$_{10}$]$^{•+}$ reacts with CH$_4$ at room temperature by hydrogen-atom transfer
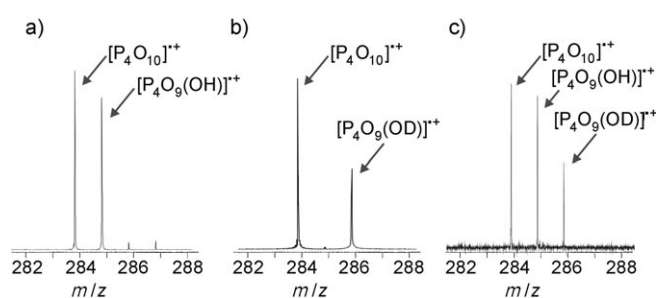
Figure 1. Mass spectra showing the reactivity of [P$_4$O$_{10}$]$^{•+}$ with a) CH$_4$, b) CD$_4$, and c) CH$_2$D$_2$ (2.2×10^{-10} mbar).

[Eq. (3)], with a rate constant of $k = 6.4 \times 10^{-10}$ cm^{3}s^{-1}molecule^{-1}; this rate corresponds to an efficiency of

$$CH_4 + [P_4O_{10}]^{•+} \rightarrow CH_3^• + [P_4O_9(OH)]^+ \qquad (3)$$
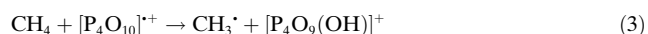
66%. The intramolecular kinetic isotope effect derived from the [P$_4$O$_{10}$]$^{•+}$/CH$_2$D$_2$ couple (Figure 1c) is 1.6. The occurrence of the reaction in Equation (3) implies that the energy of the

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newly formed O–H bond in the ionic cluster exceeds the energy of the C–H bond in methane (439 kJ mol^{-1}).[17]

Mechanistic insight into the details of the C–H bond-activation step was provided by density functional calculations. To confirm the obtained energy values, the energies of all the stationary points derived from DFT optimizations were verified by more accurate ab initio methods by using the CCSD(T) level of theory. According to the UB3LYP-based computations, the most stable isomer of the $[P_4O_{10}]^{\cdot+}$ cluster ion has a slightly distorted tetrahedral cage structure with C_s symmetry. In comparison with neutral P_4O_{10}, the removal of one electron from the P=O bond results in the elongation of one of the terminal P–O bonds in the cation from 1.46 to 1.57 Å (Figure 2). The spin density has the shape of a p orbital
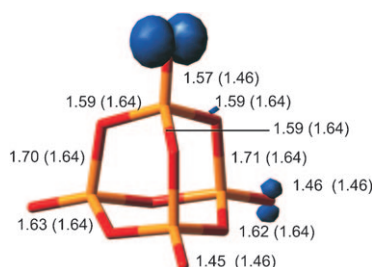
Figure 2. Lowest-energy structure calculated for $[P_4O_{10}]^{\cdot+}$ using DFT with the UB3LYP functional (yellow P, red O). The blue isosurface indicates the spin density. P–O distances for $[P_4O_{10}]^{\cdot+}$ and P_4O_{10} (in parentheses) are given in Å.

and is mainly localized at the terminal phosporyl oxygen atom. The $[P_4O_{10}]^{\cdot+}$ cluster and the $[V_4O_{10}]^{\cdot+}$ structure[9] show not only remarkable structural similarities, but also energetic features that extend to their reactions with CH_4.

The coordination of methane to the $[P_4O_{10}]^{\cdot+}$ cluster and the smooth hydrogen-atom abstraction process are associated with a significant energy gain of 162 kJ mol^{-1} (from DFT) or 168 kJ mol^{-1} (from CCSD(T); Figure 3). It is noted that no stable encounter complexes of the type $[P_4O_{10}]^{\cdot+}(CH_4)$ were
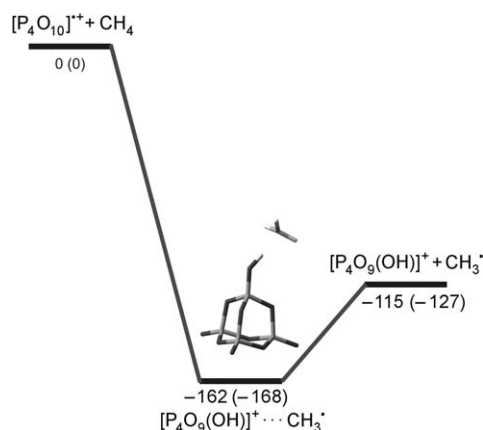
Figure 3. Energy diagram for the reaction of $[P_4O_{10}]^{\cdot+}$ and methane. The values from DFT (corresponding to the energy scale) and CCSD(T) (in parentheses) calculations are relative to the entrance channel, are corrected for zero-point energy, and given in kJ mol^{-1}.

found in the structure optimizations, which suggests that the reaction proceeds without a noticeable reaction barrier by direct hydrogen-atom abstraction to form the intermediate $[P_4O_9(OH)]^+ \cdot CH_3$. For the related $[V_4O_{10}]^{\cdot+}/CH_4$ system, molecular dynamics calculations suggested that formation of the O–H bond and cleavage of the C–H bond are complete after approximately 450 fs. In view of the quite similar potential energy surfaces of the two couples $[X_4O_{10}]^{\cdot+}/CH_4$ (X = V, P), we assume a comparable timescale of C–H bond activation for the $[P_4O_{10}]^{\cdot+}/CH_4$ system. In the intermediate $[P_4O_9(OH)]^+ \cdot CH_3$, the methyl group is very loosely coordinated to the hydrogen atom of the newly formed, phosphorous-bound hydroxy group; the reaction is completed by the loss of a $CH_3^{\cdot}$ radical concomitant with the formation of $[P_4O_9(OH)]^+$. The exothermicity, which is computed to be -115 kJ mol^{-1} (from DFT) or -127 kJ mol^{-1} (from CCSD(T)), together with the absence of kinetic barriers, are in full agreement with the experimentally observed occurrence of the reaction shown in Equation (3) at room temperature. Our combined experimental and computational studies provide the first example for the thermal activation of methane by a polynuclear metal-free oxide cation.

Experimental Section

All experiments were carried out with a Bruker APEX IV Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer 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 $[P_4O_{10}]^{\cdot+}$ was then subjected to a pulse of argon, so that the product ions were assumed to be thermalized.[18] After careful resolation and after a variable reaction delay of 0–5 seconds, the ions were detected by a standard excitation and detection sequence. The reactivity was studied by introducing methane through a leak valve at stationary pressures in the order of 2.5×10^{-10} mbar. The experimental second-order rate constants were evaluated assuming pseudo first-order kinetic approximation after calibration of the measured pressures and acknowledgment of the ion gauge sensitivities;[19] the error of the absolute rate constants is assumed to be ±50%.

All calculations for optimization were performed using the hybrid density functional theory method UB3LYP[20] with triple-ζ plus polarization basis sets TZVP.[21] 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 energy of all stationary points was computed also by single point calculations with the coupled cluster method including triple excitations CCSD(T)[22] using the same basis set TZVP. The Gaussian03 program suite was used for all the calculations.[23]

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