VIP Methane Activation

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Diatomic $[CuO]^+$ and Its Role in the Spin-Selective Hydrogen- and Oxygen-Atom Transfers in the Thermal Activation of Methane**

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Dedicated to Professor Hans-Joachim Freund on the occasion of his 60th birthday

The activation of methane and its subsequent conversion into more valuable feedstocks at ambient conditions is regarded as one of the major challenges in contemporary catalysis.[1] In this context, two different transformations are of particular interest. The first one concerns the oxidative coupling of methane (OCM) to the C_2 hydrocarbons ethane and ethylene using metal oxide based catalysts in heterogeneous catalysis;[1c,d,2] the second process is the selective oxidation of methane to methanol, which is performed in nature by the methane monoxygenase (MMO) metalloenzymes.[3] Soluble MMO (sMMO) contains a well-characterized doubly oxygen-bridged di-iron cluster; in contrast, the reactivity of particulate MMO (pMMO), after a long controversy about the nature of its active site, has been shown to depend on copper.[4]

A useful approach to investigate model systems for oxygen-containing catalysts takes advantage of state-of-the-art gas-phase experiments conducted in a mass spectrometer, in conjunction with computational studies; this combined experimental and theoretical approach provides insight into the elementary steps of these reactions at a molecular level and, thus, permits us to unravel detailed mechanistic aspects.[5] For example, the efficient gas-phase activation of methane at room temperature has been demonstrated to be brought about by a variety of systems, including transition- and main-group-metal oxides[6] as well as some selected nonmetal oxides[7] and mixed metal/nonmetal oxides;[8] based on these studies, a rather detailed understanding of the intriguing mechanistic aspects has been arrived at.

With respect to biological relevance, it was demonstrated twenty years ago that bare $[FeO]^+$ is capable of activating methane at room temperature.[9] The now well-established concept of two-state reactivity (TSR),[10] which also proved important in describing the mechanisms of metalloenzyme-mediated reactions, is in fact based on a detailed analysis of the gas-phase reactions of this simple, diatomic reagent $[FeO]^+$. Yet, only recently has a complete description of the gas-phase conversion of methane to methanol by $[FeO]^+$ been achieved; this elucidation was based on advanced gas-phase spectroscopy combined with rather high-level calculations.[11]

Further, while the detailed nature of the active copper oxide species in pMMO had been under debate for quite some time,[3,4,12] bare $[CuO]^+$ was predicted a decade ago to be a suitable, if not extremely powerful, candidate to mediate the methane to methanol conversion.[13,14] However, no gas-phase experiments with bare $[CuO]^+$ have been reported to date. The ligated cation $[Cu(O)(phen)]^+$ (phen = 1,10-phenanthroline) brings about activation of small hydrocarbons, that is, propane or butane, but it is not powerful enough to attack the thermodynamically strong and kinetically inert C–H bond of methane.[15] Owing to the relatively low dissociation energy $D_0(Cu^+–O) = 130\ kJ\,mol^{-1}$,[5a,16] it proved rather difficult to produce sufficient amounts of $[CuO]^+$ to probe its reactivity in bond-activation processes, and various attempts to generate this cationic metal oxide by, for example, electrospray ionization mass spectrometry failed.[5j,15] Thus, $[CuO]^+$ is to date the only bare transition-metal oxide cation of the first row whose reactivity towards methane has not been experimentally investigated.

Herein we present our results on 1) the successful formation of gaseous $[CuO]^+$ and 2) its reactivity towards methane at thermal conditions. Briefly, $[CuO]^+$ is generated by laser desorption/ionization from isotopically pure copper ^{63}Cu targets, suitable for the laser-vaporization/ionization source of an FT-ICR mass spectrometer in the presence of a He/N_2O plasma (for details about the instrumental setup, see the Experimental Section). As shown in Figure 1, $[CuO]^+$ brings about efficient activation of methane at room temperature both by hydrogen abstraction [Eq. (1)] and by oxygen-atom transfer [Eq. (2)]. Furthermore, the *open-shell* product cation $[CuOH]^{\bullet+}$ itself also homolytically cleaves the C–H bond of a second methane molecule, thus giving rise to the formation of a *closed-shell* water complex [Eq. (3)].[17]

$$[CuO]^+ + CH_4 \longrightarrow [CuOH]^{\bullet+} + CH_3^{\bullet} \quad (40\,\%) \quad (1)$$

$$[CuO]^+ + CH_4 \longrightarrow [Cu]^+ + CH_3OH \quad (60\,\%) \quad (2)$$

$$[CuOH]^{\bullet+} + CH_4 \rightarrow [Cu(OH_2)]^+ + CH_3^{\bullet} \quad (3)$$

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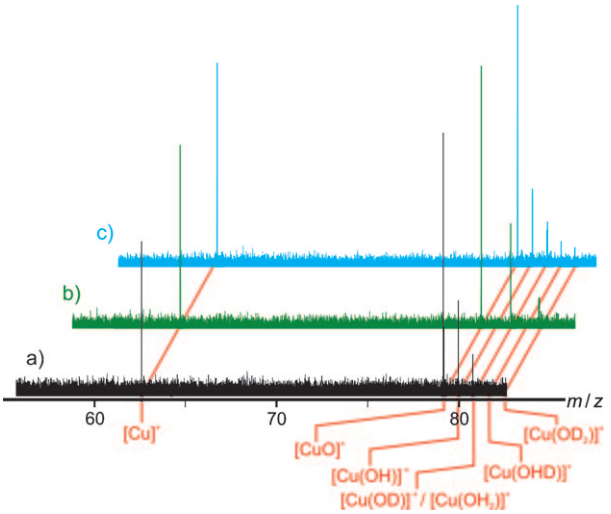

Figure 1. Mass spectra showing the reactivity of mass-selected $[CuO]^+$ with methane at 1.5×10^{-8} mbar: a) CH_4, b) CD_4, and c) CH_2D_2.

From a kinetic analysis, a rate coefficient of $k=5.3\times10^{-10}\,cm^3\,s^{-1}\,molecule^{-1}$ was derived; this value corresponds to an overall efficiency of 51%, that is, 20% for reaction (1) and 31% for reaction (2). On the basis of labeling experiments with CH_2D_2, an intramolecular KIE of 2.6 has been obtained for the hydrogen-abstraction process.[18] For the hydrogen abstraction in the related $[FeO]^+/CH_4$ system, an efficiency of 11% and a KIE of 4.6 were reported.[9] As discussed by Schröder et al.,[19] decreasing KIEs are often associated with increasing reaction efficiencies for a given type of reaction, for example, the hydrogen-atom abstraction from methane.

Further mechanistic insights into the details of the reaction are provided by quantum chemical calculations. A density functional theory (DFT) study of reactions (1) and (2) using the B3LYP functional has been presented in the literature;[13] however, the high-spin/low-spin splitting of $[Cu]^+$ reported in this study (156 kJ mol^{-1}) is largely underestimated compared to the experimental value (271 kJ mol^{-1}).[20] Curiously, a much better value (281 kJ mol^{-1}) was obtained in a different context also using the B3LYP functional but with different basis sets.[21] We decided therefore to recalculate the potential-energy surface (PES) of the reaction $[CuO]^+ + CH_4$ in the hope of providing an improved picture of the reaction mechanism, including more reliable energetic values. However, calculations at the otherwise accurate CCSD(T)[22] level of theory with moderately sized basis sets are not suited for the $[CuO]^+/CH_4$ system. Thus, we employed the complete basis set procedure CBS-QB3[23] to study the reactivity of $[CuO]^+$ towards methane. The resulting PES is shown in Figure 2.

As has been found for other late-transition-metal oxides, the high-spin, O_2-like state (triplet) corresponds to the ground state of $[CuO]^+$;[5a,j,13] the bonding situation in $[MO]^+$ (M = late 3d metal) has been described in analogy to the dioxygen molecule having biradicaloid π bonding.[5b,24] This analogy also holds true for $[CuO]^+$ with degenerate singly occupied π orbitals, which correspond to the antibonding π* orbital of

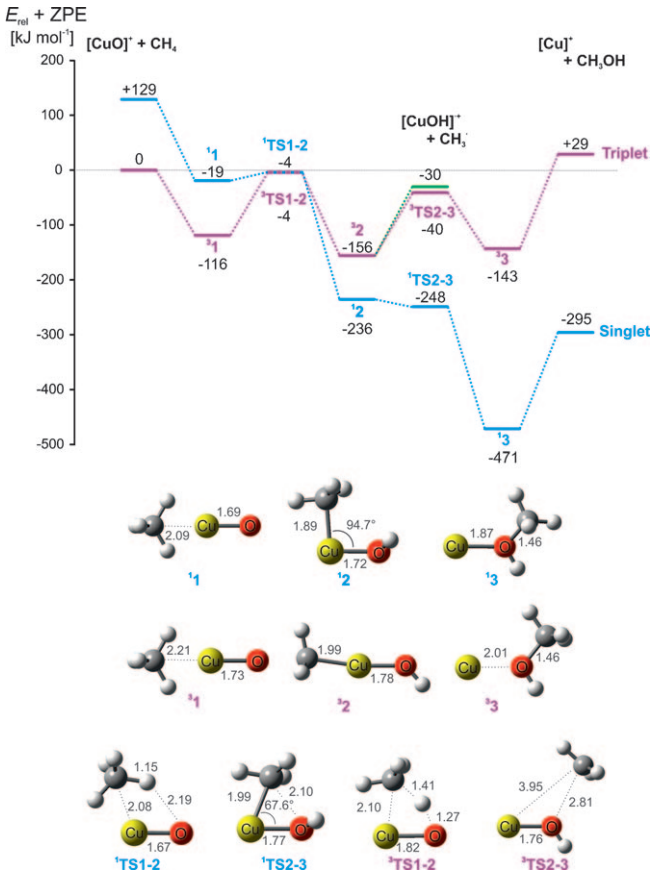

Figure 2. Potential-energy surface for the reaction of $[CuO]^+$ with CH_4 and the associated structures of the intermediates and transition structures calculated at the CBS-QB3 level of theory. Relative energies corrected for zero-point energy contributions are given in kJ mol^{-1} and relevant bond lengths in Å.

$[CuO]^+$. However, these orbitals possess a relatively strong character of the $2p_\pi$ orbital of oxygen, thus resulting in a spin density of 1.68 at oxygen and of only 0.32 at copper.[25] In contrast, σ-type bonding to both ligands prevails in intermediate **2**. As a consequence, a low-spin state is preferred energetically for **2**, and an intersystem crossing (ISC) has to take place to form the singlet-ground-state structure ^{1}**2**.

That a TSR scenario is indeed involved in the formation of methanol and $[Cu]^+$ as in Equation (2) is indicated by the finding that this reaction path is endothermic by 29 kJ mol^{-1} on the triplet surface. Thus, a reaction under thermal conditions can be ruled out, and the experimentally observed formation of methanol can only be explained by ISC to the singlet state, resulting in an overall exothermicity of −295 kJ mol^{-1}. On the triplet surface the reaction rather proceeds by spin-allowed hydrogen-atom abstraction to generate $[CuOH]^{\bullet+} + CH_3^\bullet$ via the sequence ^{3}**1**→^{3}**TS1-2**→^{3}**2**.[26] Since the two geometrically quite different transition structures ^{1,3}**TS1-2** are almost isoenergetic, the ISC to the singlet surface most likely occurs either just before or directly after passing through **TS1-2**. Furthermore, the singlet intermediate ^{1}**2** is significantly lower in energy than ^{3}**2**. From ^{1}**2**, the reaction can proceed downhill via ^{1}**TS2-3** to generate singlet

$[Cu\text{-}(CH_3OH)]^+$ (^{1}**3**) in an almost barrier-free process;[27] from ^{1}**3** CH_3OH is liberated to produce atomic $[Cu]^+$ and CH_3OH.

A minimal-energy crossing point[28] of the two potential-energy surfaces has not been located in this study; however, the remarkable branching ratio of 60% for the formation of methanol in the experiment indicates a rather efficient ISC at the crossing seam of the two PESs. Further, the close relationship between $[CuO]^+$ and $[FeO]^+$ is attested to by the fact that only for these two bare metal oxide cations are both the homolytic C–H bond scission of methane and the conversion to methanol observed.

Thus, at long last this combined experimental and computational study verifies the computationally based predictions on the remarkable reactivity of $[CuO]^+$ and clearly confirms the effective activation of methane under thermal conditions. Moreover, this investigation also demonstrates that homolytic bond activation can be brought about by metal oxides with even numbers of electrons. In $[CuO]^+$ it is the ($^3\Sigma^-$) triplet ground state, with its high unpaired spin radical density at the oxygen center, that is crucial for the hydrogen-atom transfer process, while TSR in combination with the low bond energy of $[Cu^+\text{–}O]$ enables the $CH_4 \rightarrow CH_3OH$ conversion.

Experimental Section

All 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 $[CuO]^+$ cation was produced by laser vaporization[29] of a rotating ^{63}Cu target with a 5 ns laser pulse of a frequency-doubled Nd:YAG laser (Continuum Surelite II, 10 Hz, 5 mJ pulse energy), with subsequent supersonic expansion of the hot plasma in a triggered helium/N_2O (ratio approximately 5:1) pulse. The transfer of the copper oxide clusters was accomplished by an electrostatic lens system through differential pumping stages into the ultrahigh vacuum (UHV) region; there the $[CuO]^+$ ions were mass-selected by means of the FERETS ion-ejection method[30] and stored in the ICR cell. The reactivity was studied by introducing methane by a needle leak valve at stationary pressures on the order of 1.5×10^{-8} mbar. The experimental second-order rate coefficients were evaluated assuming a pseudo-first-order kinetic approximation after calibration of the measured pressures and acknowledgment of the ion-gauge sensitivities;[31] the error of the absolute rate constants is assumed to be ±30%. The isotopically pure copper sample was purchased from STB Isotope Germany GmbH (^{63}Cu 99.3%).

All calculations were performed using complete basis set procedure CBS-QB3.[23] 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; all energetic values given herein are corrected for zero-point energy and given in kJ mol^{-1}). The CBS-QB3 approach uses the UB3LYP[32] functional coupled to the CBSB7 defined basis sets for all geometry optimizations and frequency calculations. Intrinsic reaction coordinate (IRC) calculations were performed to link all transition-state structures with the respective intermediates.[33] The spin densities for the triplet states were derived from the B3LYP calculation within the CBS method; the reactants, intermediates, and transition structures on the singlet surface correspond to closed-shell singlet species. The Gaussian09 program suite was used for the calculations.[34]

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