Gas-Phase Reactions

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The Unique Gas-Phase Chemistry of the $[AuO]^+/CH_4$ Couple: Selective Oxygen-Atom Transfer to, Rather than Hydrogen-Atom Abstraction from, Methane

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Dedicated to Professor Zvi Rappoport on the occasion of his 80th birthday

Abstract: *The thermal reaction of $[AuO]^+$ with methane has been explored using FT-ICR mass spectrometry complemented by high-level quantum chemical calculations. In contrast to the previously studied congener $[CuO]^+$, and to $[AgO]^+$, $[AuO]^+$ reacts with CH_4 exclusively via oxygen-atom transfer to form CH_3OH, and a novel mechanistic scenario for this selective oxidation process has been revealed. Also, the origin of the inertness of the $[AgO]^+/CH_4$ couple has been addressed computationally.*

Oxidation of methane constitutes an important method to convert this abundantly available feedstock into value-added commodities.[1] Among the vast number of gas-phase studies on methane activation,[2] quite a few of them describe how to achieve, via C−O coupling, the direct generation of methanol or formaldehyde.[3] For example, the diatomic transition-metal oxides MO^+ (M = Fe, Co, Ni, Cu, Pd) are able to transfer their oxygen atom to methane under the elimination of methanol;[3e,g,k–n] also, larger cluster oxides, for example, $[Al_2O_3]^+$ or $[PtAl_2O_4]^-$, oxidize methane to formaldehyde.[3b,c] In addition, in the reactions of methane with oxygen-rich cluster ions, such as $[CrO_2]^+$, $[PtO_2]^+$, and $[TaO_3]^+$, both methanol and formaldehyde can be generated.[3a,f,i] However, often these transformations compete with parallel reactions, and only in a few cases "doping" the cluster oxides helps to increase the chemoselectivity.[2a,4] Exclusive formation of methanol has been observed in the reactions of $[CoO]^+$ and $[NiO]^+$ with methane; for $[CoO]^+$, however, this process takes place with a rather low efficiency.[3e,m]

Herein, we report that bare $[AuO]^+$ is capable of activating methane selectively by transferring its oxygen atom to methane to form methanol. This behavior is in distinct contrast to the reactivity of its lighter congener $[CuO]^+$, which brings about both spin-selective oxygen- and hydrogen-atom transfers (OAT[5] and HAT,[6] respectively).[3d] Herein, we will describe mechanistic aspects for the thermal reaction of the couple $[AuO]^+/CH_4$ and discuss the root cause for this remarkably selective oxidation. In addition, we present the potential energy surface for the $[AgO]^+/CH_4$ system.

Mass-selected and thermalized $[AuO]^+$ reacts with CH_4 to afford Au^+ as the single product ion, Figure 1a and Equation (1); the reaction efficiency amounts to $\phi = 8\%$, relative to the collision rate,[7] with a rate constant of $k = (5 \pm 1.5) \times 10^{-11}$ $cm^3\,molecule^{-1}\,s^{-1}$. Owing to the uncertainty in the determination of the absolute pressure, an error of ±30% is associated with these measurements.[3g] In the reaction of $[AuO]^+$ with CD_4, the rate constant decreases to $k = (2.5 \pm 1.5) \times 10^{-11}$ $cm^3\,molcule^{-1}\,s^{-1}$; thus, an intermolecular kinetic isotope effect $KIE = k_H/k_D = 2.0$ is operative.

$$[AuO]^+ + CH_4 \rightarrow Au^+ + CH_3OH \qquad (1)$$

Next, the reaction mechanisms were interrogated by quantum chemical calculations. The potential-energy surfaces

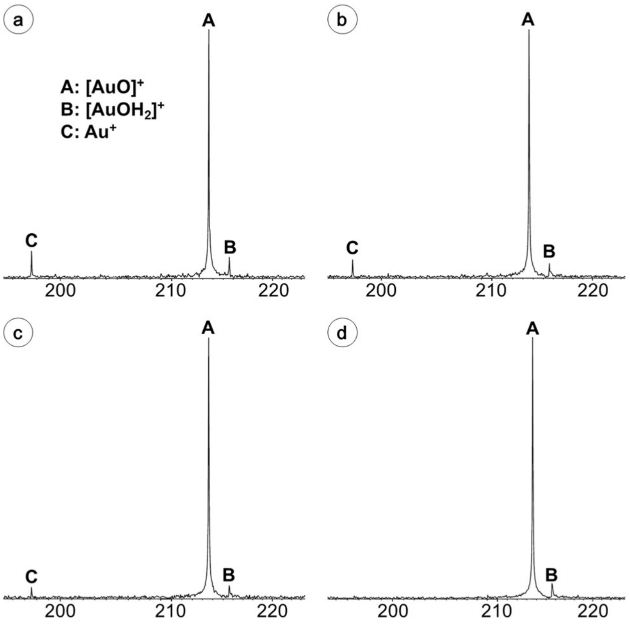

Figure 1. Mass spectra for the thermal reactions of mass-selected $[AuO]^+$ with methane: **a**) CH_4, **b**) CH_2D_2, **c**) CD_4, and **d**) Ar ($p = 8 \times 10^{-8}$ mbar; reaction delay 1.5 s); the signal labeled as **B** arises from the reaction of $[AuO]^+$ with background water; more technical details are provided in the Supporting Information.

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(PESs) of the most favorable reaction pathways as well as some structural information of relevant species generated in the reactions of $[AuO]^+$ with CH_4 are shown in Figure 2.

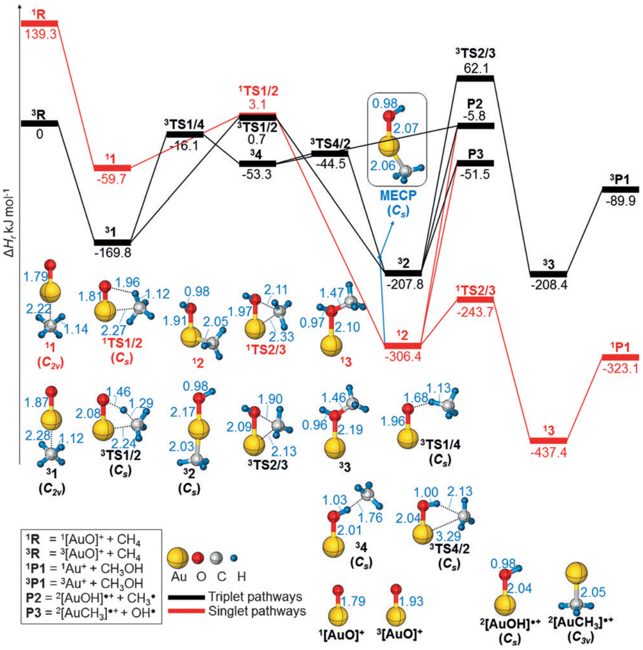

Figure 2. PES and selected structural information for the reaction of $[AuO]^+$ with CH_4 as calculated at the CCSD(T)/BSII//B2GP-PLYP/BSI level of theory. Zero-point corrected energies are given in kJ mol^{-1} and bond lengths in Å; charges are omitted for the sake of clarity.

There are two spin states of $[AuO]^+$ to be considered. While triplet $^3[AuO]^+$ corresponds to the ground state, as will be shown the excited singlet state also plays a role in the $[AuO]^+/CH_4$ system. On the singlet PES, only one pathway has been located (PES given in red in Figure 2). Starting from an encounter complex **^{1}1**, in which methane is tightly bound to the gold atom in an η^3 manner, the oxidative insertion of $^1[AuO]^+$ into the $H_3C{-}H$ bond takes place via **^{1}TS1/2** to form the rather stable intermediate **^{1}2**. Cleavage of the Au−X (X = C or O) bonds of **^{1}2** results in the generations of either $^2[AuOH]^{\bullet+} + CH_3^{\bullet}$ (**P2**) or $^2[AuCH_3]^{\bullet+} + OH^{\bullet}$ (**P3**); however, the rebound of the methyl group via **^{1}TS2/3** to form the methanol complex **^{1}3** is much more favored energetically. The so formed intermediate **^{1}3** liberates its methanol ligand in an overall rather exothermic process to generate **^{1}P1**. This “insertion–rebound” pathway has also been located on the ground-state triplet surface. As shown in Figure 2, the transformations along the sequence **^{3}R**→**^{3}1**→**^{3}2**→**^{3}3**→**^{3}P1** are structurally rather similar with the one located on the singlet surface. However, since both transition states **^{1}TS1/2** and **^{3}TS1/2** are higher in energy as compared to the ground-state entrance channel (**^{3}R**), neither of these pathways is thermally favored. In fact, none of the products **P$_{1,2,3}$** should be observed experimentally! However, an alternative, novel reaction pathway, which is accessible under ambient conditions, has been located on the triplet surface; this route had not been previously considered in the theoretical investigation of the related $[CuO]^+/CH_4$ system.[3d,8] Starting from **^{3}1**, a hydrogen atom can be transferred from methane to the oxygen atom via **^{3}TS1/4** to form intermediate **^{3}4**; in this intermediate, the methyl radical (the spin density at the C atom amounts to 0.88) is interacting with the newly generated hydroxy group. However, rather than liberating $CH_3^{\bullet}$ to form $^2[AuOH]^{\bullet+}$, the methyl group rebounds to the gold atom via **^{3}TS4/2** to generate the Au^{III} insertion complex **^{3}2**. It is this very path (**^{3}1**→**^{3}TS1/4**→**^{3}4**→**^{3}2**) which is crucial for the generation of Au^+ and CH_3OH.

If the triplet ground state of the $[AuO]^+/CH_4$ system were not to interact with the excited singlet state, the energetically most favorable reaction path corresponds to **^{3}R**→**^{3}1**→**^{3}4**→**^{3}2**→**P3** and, thus, gives rise to the formation of $^2[AuCH_3]^{\bullet+}$ and an OH radical (**P3**). Generation of methanol via **^{3}R**→**^{3}1**→**^{3}4**→**^{3}2**→**^{3}3**→**^{3}P1** cannot compete. Yet, it is CH_3OH which is liberated from $[AuO]^+/CH_4$, and neither **P2** nor **P3** are formed (Figure 1)! Thus, most likely a two-state reactivity (TSR) scenario[9] is operative in the formation of methanol due to an interplay of the triplet/singlet surfaces. To probe this further, the minimum energy crossing point (MECP)[10] has been located on the seam where the singlet and triplet surfaces intersect, and the MECP has been located near **^{3}2** on the PES (Figure 2). Decreasing the O-Au−C bond angle of the MECP results in the formation of **^{1}2**; this intermediate is 100 kJ mol^{-1} lower in energy compared to the MECP. Thus, the energetically most favorable pathway for the reaction of $[AuO]^+$ with CH_4 corresponds to **^{3}R**→**^{3}1**→**^{3}4**→MECP→**^{1}2**→**^{1}3**→**^{1}P1**. In line with the experimental findings, all other reaction channels are much less competitive energetically. In addition, the absence of signals for $[AuOH]^{\bullet+}$ (**P2**) and $[AuCH_3]^{\bullet+}$ (**P3**), which were to be generated under the elimination of $CH_3^{\bullet}$ and $OH^{\bullet}$, respectively, if spin crossing did not occur, indicates a rather efficient intersystem crossing (ISC) between the two spin states. In contrast, ISC in the previously studied $[CuO]^+/CH_4$ system is less efficient; as a consequence, the HAT reaction which is confined to the triplet ground-state PES of $[CuO]^+/CH_4$ competes with the OAT process; the OAT takes place in a TSR scenario involving a triplet–singlet crossing.

Further, for the $[AuO]^+/CH_4$ couple, we note that according to Figure 2 the transition structure **^{3}TS1/4**, in which the C−H bond of methane is cleaved, corresponds to the rate-limiting step in the formation of CH_3OH from $[AuO]^+/CH_4$. This is in line with a KIE of 2.0 as determined experimentally. In addition, as suggested by a Reviewer, we have calculated the pathways for the conceivable productions of the pairs formaldehyde/molecular hydrogen and methylene/water as an alternative to the formation of CH_3OH; however, these processes are much less favored energetically (for more details, see Supporting Information).

To obtain an even deeper understanding of this selective oxygen-atom transfer reaction, the electronic structures of the intermediates and transition structures of the pathways, shown in Figure 2, have been analyzed. As suggested previously,[11] the bonding pattern of ground-state $^3[AuO]^+$ can be described by a donor–acceptor model. Thus, the oxygen atom donates an electron pair from the p_z orbital to the empty 6s orbital of Au^+, and the electrons from the p_x and p_y orbitals of the oxygen atom singly occupy two weakly antibonding π* molecular orbitals. As the π back-donation from the d orbitals of Au is minor,[11] a spin density of 1.92 at oxygen and of only 0.08 at gold results. This bonding pattern is similar to the one previously described for other diatomic oxides $[MO]^+$ (M = late 3d transition metal, including Cu), in which two biradicaloid π* orbitals are also present.[12] In intermediate **2**, however, gold is twofold coordinated, and the singlet state corresponds to the electronic ground state. Thus, while in **^{1}2** both ligands are bound via covalent σ(Au−C) and σ(Au−O) bonds, respectively, the Au−O bond orbital in **^{3}2** is only singly occupied, resulting in a relatively weak BDE-($(H_3C)Au^+{-}OH$) of 156 kJ mol^{-1}; accordingly, the Au−O bond is much longer in **^{3}2** compared to **^{1}2** (2.17 Å versus 1.91 Å); also, the Au−C bond is slightly elongated (2.05 Å versus 2.03 Å for **^{3}2** and **^{1}2** respectively). Further, the calculated BDE($(HO)Au^+{-}CH_3$) (301 kJ mol^{-1}) is much higher than BDE($Au^+{-}CH_3$) (209 kJ mol^{-1}[13]), that is, the presence of the hydroxy ligand strengthens the Au−C bond in intermediate **2**. It is also notable that the higher relative energy of **P2** as compared to **P3** indicates BDE($Au^+{-}OH$) (63 kJ mol^{-1}[14]) < BDE($Au^+{-}CH_3$); given that for both $[AuCH_3]^{\cdot+}$ and $[AuOH]^{\cdot+}$ the ligands donate an electron to the empty 6s orbital of Au^+, most likely the lower binding energy of this 6s orbital results from the higher electronegativity of OH such that it is reluctant to share its electron density with the rather electronegative gold core.[15]

In addition to the different product pattern for the two systems $[MO]^+/CH_4$ (M = Cu, Au), $[AuO]^+$ reacts less efficiently ($\phi = 8\,\%$) than $[CuO]^+$ ($\phi = 51\,\%$).[3d] This is somewhat in contrast to the higher BDE($Cu^+{-}O$) (130 kJ mol^{-1}[16]) as compared to BDE($Au^+{-}O$) (109 kJ mol^{-1}[11]); thus, the reasons for the different efficiencies are more complex and are likely to be based on detailed differences in the individual PESs of the reaction paths for both species, as discussed recently for other systems in a broader context.[2b]

Finally, as suggested by a reviewer we tried to produce also $[AgO]^+$ under the conditions employed for generating $[AuO]^+$ or using various ESI procedures (see Supporting Information for details). However, in line with recent independent experiments by Roithová and co-workers, all attempts failed.[17] In any case, according to our theoretical findings, $[AgO]^+$ is not expected to react with CH_4 under ambient conditions. As shown in Figure 3, for both spin states of $[AgO]^+$ the transition states of the initial steps of methane activation are energetically well above the entrance channel of the $[AgO]^+/CH_4$ couple. Further, as the MECP for the triplet–singlet conversion is located after the rate-limiting **^{3}TS5/6**, a TSR scenario would be of no help with the consequence that C−H bond activation of methane is predicted not to occur under ambient conditions by $[AgO]^+$.

When comparing the thermal reaction of CH_4 with the three diatomic coinage-metal oxide cations $[MO]^+$ (M = Cu, Ag, Au), one cannot escape the conclusion that in spite of some commonalities, once more R. Hoffmann's dictum "*The same and not the same*" holds true:[18] $[CuO]^+/CH_4$ is reactive giving rise to both HAT and OAT, $[AgO]^+$ is predicted to be inert, and $[AuO]^+/CH_4$ is both reactive and selective in that only CH_3OH is generated.

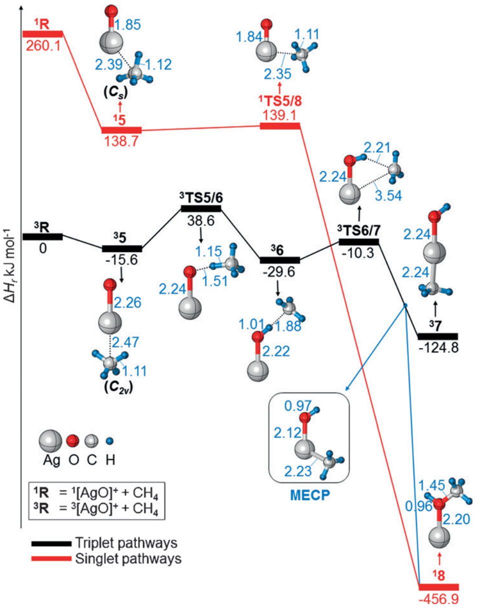

Figure 3. PES and selected structural information for the reaction of $[AgO]^+$ with CH_4 as calculated at the CCSD(T)/BSII//B2GP-PLYP/BSI level of theory. Zero-point corrected energies are given in kJ mol^{-1} and bond lengths in Å; charges are omitted for the sake of clarity.

A similar situation of reactivity changes, in particular of mechanistic aspects, along a group of the Periodic Table had been reported for the $[MH]^+/CH_4$ couples (M = Ni, Pd, Pt) in the thermal ligand exchange, Equation (2).[19]

$$[MH]^+ + CH_4 \rightarrow [M(CH_3)]^+ + H_2 \qquad (2)$$

In summary, we have demonstrated that the thermal activation of methane by $[AuO]^+$ can be achieved; further, the exclusive formation of CH_3OH can be traced back to a novel mechanistic scenario. While a hydrogen-atom transfer from methane to $[AuO]^+$ and the subsequent formations of $[AuOH]^{\cdot+}$ and $[AuCH_3]^{\cdot+}$ under the eliminations of $CH_3^{\cdot}$ and $OH^{\cdot}$, respectively, are energetically possible on the triplet-ground-state surface of $[AuO]^+/CH_4$, owing to an efficient ISC to the singlet PES the occurrence of OAT to produce CH_3OH dominates. While the PESs for the $[AuO]^+/CH_4$ couple have a few common features with the PESs of its lighter congeners $[CuO]^+$ and $[AgO]^+$, for the $[CuO]^+/CH_4$ couple, HAT takes place in competition with OAT as a result of a less efficient ISC, while $[AgO]^+$ is inert towards CH_4.

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