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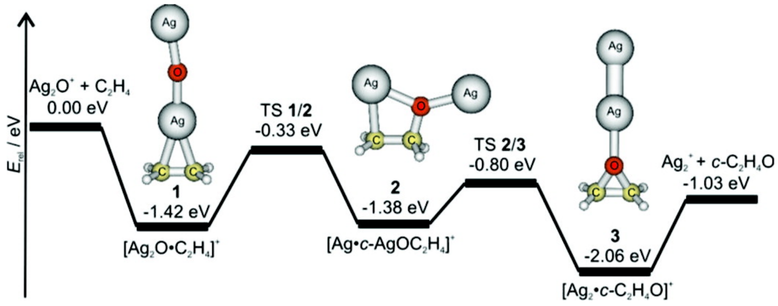

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Gas-Phase Models for Catalysis: Alkane Activation and Olefin Epoxidation by the Triatomic Cation Ag_2O^+

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Abstract: Electrospray ionization of aqueous silver nitrate is used for the preparation of the disilver-oxide cation Ag_2O^+ in the gas phase. The mass-selected cation is capable of activating C−H bonds of simple alkanes other than methane via H-atom abstraction, i.e., $Ag_2O^+ + R{-}H \rightarrow Ag_2OH^+ + R^\bullet$ ($R = C_2H_5, C_3H_7, C_4H_9$). Clean O-atom transfer from Ag_2O^+ is observed with ethene as a neutral reagent, whereas oxygenation and allylic C−H abstraction compete in the case of propene. The gaseous Ag_2O^+ cation can thus be regarded as a minimalist model for the problems associated with the silver-mediated epoxidation of olefins more complex than ethene itself. The experimental findings are fully supported by the results of quantum chemical studies, thereby providing deep mechanistic insight into the reactions in the idealized gas phase, which also might have implications for further improvements in applied catalysis.

Introduction

Metallic silver is used as a powerful catalyst for the production of ethylene oxide from ethene and oxygen with an annual volume of billions of U.S. dollars.[1] In the technical process, however, the desired epoxidation is accompanied by a considerable amount of combustion, which not only lowers the product yields but also causes substantial problems associated with heat evolution. Further, extension to other substrates, particularly propene, would be very useful but encounters severe difficulties because allylic C−H bond activation competes with the desired epoxidation; some recent developments appear promising in this respect.[2,3] Mechanistic studies on the silver-mediated epoxidation of olefins and in particular detailed insight into the elementary steps might provide valuable assistance for the further optimization of the catalysts. In this context we note that even minor improvements can have a huge impact due to the large volume of the production of ethylene oxide. An increase of 1% in selectivity, for example, would not only increase the product yield but also lower the byproducts as well as the heat production in the reactor. Specifically for the silver-mediated epoxidation of ethene, it has been suggested that *"epoxidation and combustion go through an unidentified common intermediate in the rate-limiting step"*.[1] Here, we report the generation of the triatomic cluster cation Ag_2O^+ which might be considered as a functional model for silver-mediated oxidation catalysis,[4] and we also provide a minimalist suggestion for the common intermediate.[5] The highly reactive Ag_2O^+ cation[6] is accessible in the gas phase by electrospray ionization (ESI)[7] of an aqueous solution of silver(I) nitrate at appropriate conditions.[8]

Experimental and Theoretical Details

The experiments were performed with a tandem mass spectrometer with QHQ configuration (Q: quadrupole, H: hexapole) equipped with an electrospray-ionization (ESI) source as described elsewhere.[9] Briefly, the ions of interest are generated via ESI of an aqueous solution of $AgNO_3$, mass-selected using Q1, and allowed to interact with the neutral gases of interest at a pressure of ca. 10^{-4} mbar, and the ionic products are then mass-analyzed using Q2. For collision-induced dissociation experiments, xenon was used as a collision gas, and the interaction energy in the hexapole was varied between $E_{lab} = 0$ to 20 eV. The bimolecular ion/molecule reactions were studied by introducing appropriate neutral compounds to the hexapole collision cell at an

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(6) Formation of Ag_2O^+ from bare Ag_2^+ and O_2 has been reported in the literature, but thermochemically, the high bond energy of $D(Ag_2^+ - O) \geq 5.16$ eV which would be required for O-atom loss from O_2 appears rather unexpected (see text). In fact, the mass resolution in these previous measurements might have been too low for definitive conclusions. See: Socaciu, L. D.; Hagen, J.; Heiz, U.; Bernhardt, T. M.; Leisner, T.; Wöste, L. *Chem. Phys. Lett.* **2001**, *340*, 282.

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interaction energy nominally set to 0 eV for which thermal reactivity can be assumed.[10,11] In general, the pressure of the neutral reactant was kept low enough (about 2×10^{-4} mbar) to ensure single-collision conditions, but in selected cases the pressure was increased in order to deliberately allow the occurrence of consecutive reactions.[12] The assignment of all reactions was confirmed by careful consideration of the observed isotope envelopes and additional neutral-gain and neutral-loss scans.[10a] The (acetone)Ag^+ cation mentioned below was prepared in good yields by ESI of aqueous $AgNO_3$ containing ca. 1% of acetone.

The calculations were performed using the density functional method MPW1PW91[13] in conjunction with the SDD basis set for silver and 6-311+G(2d,p) basis sets for the other atoms as implemented in the Gaussian 03 suite.[14] For all optimized structures, frequency analyses at the same level of theory were used in order to assign them as genuine minima or transition structures on the potential-energy surface (PES) as well as to calculate zero-point vibrational energies (ZPVEs). The relative energies (E_{rel}) of the structures given below refer to energies at 0 K. The kinetic isotope effect for C−H(D) bond activation of ethane by Ag_2O^+ was estimated from the data of the computed transition structures using Rice−Ramsperger−Kassel−Marcus (RRKM) theory[15] by direct counting of quantum states as a functions of internal energy and rotational eigenvalues;[16] rotations were treated adiabatically.[17] The obtained microcanonical rate constants, k(E,J,K), were averaged, assuming thermal distribution of rotational states at 298 K to finally obtain canonical rate constants k(E).[18]

Results and Discussion

Generation of the Ag_2O^+ Cation. At soft conditions of ionization, ESI of aqueous $AgNO_3$ affords the solvated silver(I) cation $Ag(H_2O)_2^+$ as the leading mononuclear species; also the multiply hydrated ions $Ag(H_2O)_n^+$ ($n = 3, 4$) are observed at mildest conditions.[19] In addition, small polynuclear clusters with the formal composition $[Ag(H_2O)_2^+ \cdot n\ AgNO_3]$ are observed ($n = 1-3$), which can easily be recognized by their characteristic isotope patterns.[20] At gradually enforced ionization conditions,[21] these ions expel the coordinated solvent molecules[12] or undergo cluster degradation via loss of neutral $AgNO_3$, as expected (e.g., reaction 1a). As a side reaction, however, the unsolvated dinuclear silver cluster $Ag_2NO_3^+$ permits the formation of Ag_2O^+ according to reaction 1b, in which the nitrato ligand serves as an O-atom transfer reagent.[22,23] Formation of Ag_2^+ (reaction 1c) occurs as another minor channel; the branching between reactions 1a, 1b, and 1c amounts to about 87:8:5 at a collision energy of 6 eV (given in the center-of-mass frame, collision gas: xenon).[24]

$$Ag_2NO_3^+ \rightarrow Ag^+ + AgNO_3 \qquad (1a)$$

$$\rightarrow Ag_2O^+ + NO_2^{\bullet} \qquad (1b)$$

$$\rightarrow Ag_2^+ + NO_3^{\bullet} \qquad (1c)$$

While the yields of gaseous Ag_2O^+ are thus limited, the sensitivity of the experiment is far good enough for subsequent reactivity studies. Further, collision-induced dissociation of mass-selected Ag_2O^+ affords Ag^+ as the only significant ionic product, presumably associated with the formation of neutral AgO.[25,26]

Gas-Phase Thermochemistry of Ag_2O^+. Before addressing the reactivity studies, it is instructive to summarize the literature knowledge about the thermochemistry of gaseous silver-oxide cations and related species and also present the results of our theoretical screening (Table 1). Gaseous silver-oxide ions have repeatedly been observed upon sputtering of silver salts or oxidized silver surfaces.[24,27] For the mononuclear species, Chen and Armentrout determined $D(Ag^+ - O) = 1.23$ eV.[28] Brechignac and co-workers have performed systematic studies of Ag/O cluster ions.[26,29,30] With regard to Ag_2O^+, their theoretical data suggest an oxygen bond energy of $D(Ag_2^+ - O) = 2.79$ eV,[26] which is fully consistent with the reactivity data reported below.

For an improved understanding of the generation of the Ag_2O^+ cation, we investigated the fragmentation of $[Ag_2NO_3(H_2O)_2]^+$ by means of density functional theory (DFT). The precursor ion $[Ag_2NO_3(H_2O)_2]^+$ bears a structure with a bridging nitrato ligand and terminal water ligands on both silver atoms. Removal of the first water ligand in $[Ag_2NO_3(H_2O)_2]^+$ requires 0.98 eV and is associated with a change to η^2-coordination of the non-hydrated silver cation to the bridging nitrato ligand. Loss of the second water molecule requires 1.03 eV to afford the bare $Ag_2NO_3^+$ cation, in which both silver atoms are bound to the nitrate in an η^2-fashion. Dissociation of $Ag_2NO_3^+$ according to reactions 1a−1c requires 2.06, 2.47, and 2.88 eV,

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[20] Calculated using the Chemputer made by M. Winter, University of Sheffield; see: http://winter.group.shef.ac.uk/chemputer/.

[21] In ESI, the ionization conditions can be varied systematically by adjusting the accelerating potentials in the medium-pressure section of the ESI source (ref 8). Often, increase of the so-called cone voltage leads to harder ionization conditions via multiple energizing conditions, but the details may differ for ESI sources from different manufacturers.

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[24] Occurrence of reaction 1c has been proposed earlier, but no mass selection of Ag_2O^+ was performed in that work, see: Flurer, R. A.; Busch, K. L. *J. Am. Chem. Soc.* **1991**, *113*, 3656.

[25] For Ag_nO^+ clusters, loss of atomic oxygen was also observed as a favorable channel; however, the clusters were not mass selected, and expulsion of neutral AgO might thus have escaped detection (ref 26). Also in the accompanying theoretical study, loss of neutral AgO was not considered.

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Table 1. Computed Energies (Total Energies in Hartree and Properties Given in eV at 0 K) of $[Ag_2NO_3(H_2O)_2]^+$ and Its Relevant Fragments, the Thermochemical Properties Derived Thereof, and Available Literature Data for Comparison

	E_{0K}	property (in eV)	literature values
Ag	−147.001497		
Ag^+	−146.716561	$IE(Ag) = 7.75$	7.576[28]
AgO	−222.136568	$D(Ag - O) = 1.75$	2.25 ± 0.22[28]
$AgNO_3$	−427.320104	$D(Ag - NO_3) = 2.42$	
$Ag_2NO_3^+$	−574.112394	$D(Ag^+ - AgNO_3) = 2.06$	
$[Ag_2NO_3(H_2O)]^+$	−650.564571	$D(Ag_2NO_3^+ - H_2O) = 1.03$	
$[Ag_2NO_3(H_2O)_2]^+$	−727.014918	$D(Ag_2NO_3(H_2O)^+ - H_2O) = 0.98$	
Ag_2^+	−293.777032	$D(Ag^+ - Ag) = 1.60$	1.72 ± 0.04[31]
Ag_2O[a]	−369.198498	$D(Ag_2 - O) = 1.94$	
Ag_2O^+	−368.941510	$D(Ag_2^+ - O) = 2.55$	2.79,[b] >5.1[c]
		$IE(Ag_2O) = 6.99$	
Ag_2OH^+	−369.617538	$D(Ag_2^+ - OH) = 2.95$	
		$D(Ag_2O^+ - H) = 4.69$	
H	−0.50365930		
O	−75.0707297		
OH	−75.7321531	$D(O - H) = 4.29$	4.42[d]
H_2O	−76.4142233	$D(HO - H) = 4.85$	5.16[d]
NO_2	−205.080092	$D(Ag_2O^+ - NO_2) = 2.47$	
NO_3	−280.229636	$D(Ag_2^+ - NO_3) = 2.88$	

[a] For an earlier theoretical study of Ag_2O, see: Dixon, D. A.; Gole, J. L. *Chem. Phys. Lett.* **1992**, *189*, 390. [b] Precise value according to Figure 6 in ref 26 (personal communication: C. Bréchignac, Orsay, France). [c] Lower limit implied by the reported formation of Ag_2O^+ from Ag_2^+ and O_2, see ref 6. [d] Taken from the NIST Chemistry WebBook database: http://webbook.nist.gov/chemistry/.

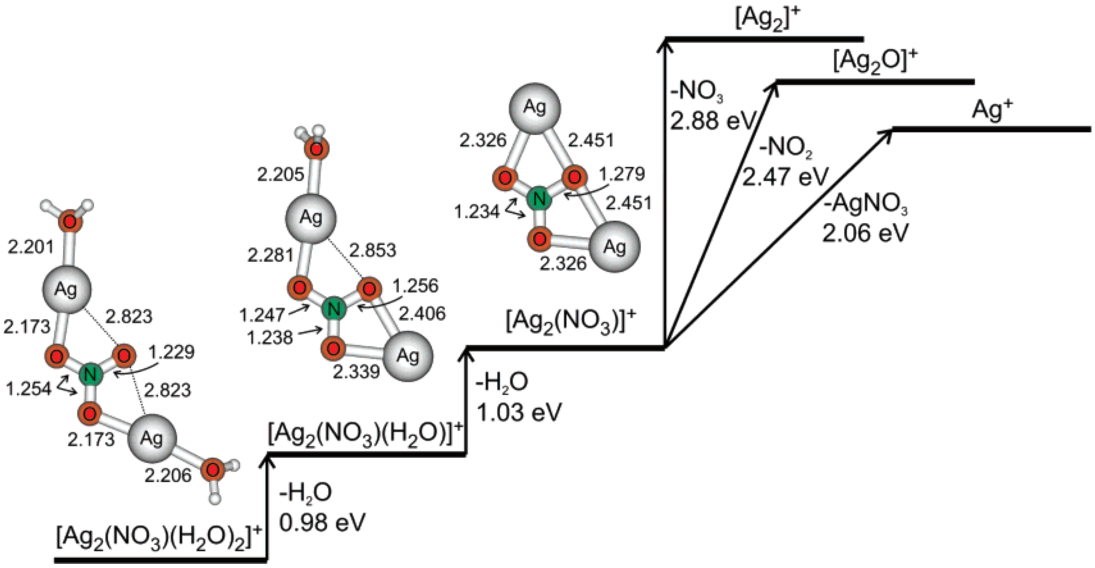

Figure 1. Calculated structures of $[Ag_2NO_3(H_2O)_2]^+$ and its relevant fragments and the associated energetics (in eV); selected bond lengths given in Å.[32]

respectively, fully consistent with the branching ratios observed experimentally.[32] For illustration, these energetics and sketches of the computed structures are summarized in Figure 1. In addition, we note the considerable hydrogen affinity of the Ag_2O^+ cation which amounts to about 4.7 eV and is thus in the order of the strength of typical C−H bonds in organic molecules.

As far as previous reactivity studies of cationic silver clusters in the gas phase are concerned, three investigations are particularly worth mentioning in the present context. Cassady and co-workers investigated reactions of Ag_n^+ clusters ($n = 1-5$) with several small molecules,[33] and more recently, Manard et al.[34] examined the reactions of Ag_2^+ with alkenes. In all studies, a facile dissociation of the dimeric cluster was observed upon approach of the neutral reagents, which can serve as a better ligand for Ag^+ than atomic silver. In the gas-phase reactions of Ag_2O^+, we might thus expect similar cluster cleavages.

Reactions of Ag_2O^+ with Alkanes. Given the interest in silver-mediated oxidation catalysis, the ion/molecule reactions of Ag_2O^+ with several simple hydrocarbons (R−H) were investigated. To this end, the Ag_2O^+ cation generated upon ESI according to reaction 1b was mass selected and allowed to interact with neutral hydrocarbon molecules admitted to the hexapole collision cell under thermal conditions. In the case of methane as a neutral reagent, no significant reactivity is observed.[35] For the saturated hydrocarbons, ethane, propane, and *n*-butane, H-atom abstraction takes place exclusively to yield

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Table 2. Bimolecular Rate Constants,[a] Branching of H- and D-Atom Transfer,[b] and Reaction Efficiencies[c] for the Reactions of Mass-Selected Ag_2O^+ with Selected Alkanes

	k_r (10^{-10} cm^3 s^{-1})	Ag_2OH^+	Ag_2OD^+	ϕ (%)
CH_4	<0.004	n.r.		<0.04
C_2H_6	0.83	100		8.7
CH_3CD_3	0.59	69	31	6.4
C_3H_8	1.89	100		19
$CH_3CD_2CH_3$	1.16	67	33	12
$CD_3CH_2CD_3$	1.47	68	32	15
C_3D_8	0.80		100	9.2
n-C_4H_{10}	1.69	100		17

[a] Evaluated by anchoring the relative rate constants of the reactions using the absolute values for the reactions of FeO^+ and Pt^+, see refs 22d and 38. The errors of the absolute and relative rate constants are estimated to ±40% and ±10%, respectively. [b] Branching ratios normalized to $\Sigma = 100$ with an error of ±3. [c] Overall reaction efficiency defined as rate constant relative to the gas-kinetic collision rate, $\phi = k_r/k_c$.

the Ag_2OH^+ cluster as ionic product concomitant with liberation of the corresponding alkyl radical (reaction 2).

$$Ag_2O^+ + R{-}H \rightarrow Ag_2OH^+ + R^{\bullet} \qquad (2)$$

$$R = C_2H_5, C_3H_7, C_4H_9$$

As already observed in many earlier studies on the C−H− and C−C bond activations by gaseous, bare, and ligated metal ions,[4,36,37] the rate constants and the reaction efficiencies for the H-atom abstraction by Ag_2O^+ increase with the size of the alkane (Table 2). Given this expected trend, our studies were not extended to more complex hydrocarbon substrates because the additional data which were provided are anticipated to be of limited insight as far as oxidation catalysis in general is concerned.

Additional valuable insight into the reaction mechanism is provided by consideration of the kinetic isotope effects (KIEs) associated with H(D) atom abstraction from the (partially) deuterated alkanes. In the case of CH_3CD_3, only activation of a primary C−H(D) bond is possible. The ratio of Ag_2OH^+ and Ag_2OD^+ formed in the reaction of Ag_2O^+ with CH_3CD_3 thus leads to a KIE of 2.20 ± 0.06. Propane bears six primary and only two secondary C−H bonds. The Ag_2OH^+/Ag_2OD^+ ratios of the deuterated propanes therefore result from an interplay of the regiochemistry of the bond activation, statistical effects, and the associated KIEs. Already the initial inspection of the data indicates that the reaction of Ag_2O^+ provides an example for an effect known as isotopically sensitive branching:[39] with $CH_3CD_2CH_3$ the major product corresponds to Ag_2OH^+ and hence activation of a primary C−H bond, while Ag_2OH^+ also prevails for $CD_3CH_2CD_3$ and thus indicates a preferential activation of a secondary C−H bond. This seeming paradox is resolved if the KIEs are large enough to affect the regiochemistry of the reactions of the deuterated substrates. Another notable observation is that the overall reaction efficiency is significantly lower for $CH_3CD_2CH_3$ compared to that for $CD_3CH_2CD_3$ (12 vs 15%, Table 2). Using kinetic modeling, such a situation can be analyzed in a quantitative manner.[40] In the first simple model, we adopt the KIE derived for ethane and use it for both primary and secondary C−H(D) bonds in propane, while fitting the branching between activation of primary and secondary C−H(D) bonds, k_{prim} and k_{sec}, respectively, to the experimental data. As shown for model 1 in Table 3, this approach can already reproduce the measured ion abundances quite well, except for the drop in the rate constant in the case of $CH_3CD_2CH_3$ which is not covered in the modeled data.

Table 3. Measured and Modeled Reaction Efficiencies ϕ_i and Branching of Ag_2OH^+ and Ag_2OD^+ in the Reactions of Mass-Selected Ag_2O^+ with Propane Isotopologues

	experiment	model 1	model 2
		$k_{prim} = 0.49$	$k_{prim} = 0.44$
		$k_{sec} = 0.51$	$k_{sec} = 0.56$
		KIE = 2.20	$KIE_{prim} = 1.68$
			$KIE_{sec} = 2.59$
C_3H_8	19%/100/−	19%/100/−	19%/100/−
$CH_3CD_2CH_3$	12%/67/33	12%/68/32	12%/67/33
$CD_3CH_2CD_3$	16%/68/32	12%/70/30	16%/68/32
C_3D_8	9%/− /100	9%/− /100	9%/− /100

In the refined model 2, different KIEs are allowed for the primary and secondary C−H(D) bonds in propane, and with this set of flexibility, the fit can reproduce all data within the experimental error. As expected from the inspection of the raw data in Table 2, notably different KIEs for primary and secondary C−H bonds are required in the modeling in order to account for the drop in overall reaction efficiency (i.e., $KIE_{prim} = 1.7$ versus $KIE_{sec} = 2.6$). After correction for the number of hydrogen atoms in primary and secondary positions, the relative rate constants k_{prim} and k_{sec} convert to a 1:3.8 preference for the activation of the secondary C−H bonds in propane which is consistent with the larger KIE of this channel.

Compared to other C−H bond activations by gaseous metal-oxide ions, these KIEs can be classified as being moderate. Thus, C−H bond activation of methane by FeO^+ is associated with KIE = 4.6;[41] for the activation of ethane by $OFeOH^+$ a KIE of about 3.5 has been derived.[42] Values similar to that for Ag_2O^+ have been observed in the reactions of CH_2D_2 with MgO^+ (KIE = 2.1)[22c] and $MoO_3{}^+$ (KIE = 2.3).[43] However, in the case of the $V_4O_{10}{}^+/CH_2D_2$ system—which can be regarded as a prototype of a simple H-atom abstraction mechanism—the KIE amounts to only 1.35,[44] which is close to the KIE of about 1.3 for the H(D)-atom abstraction from methane by free OH radicals.[45] Likewise, a KIE of about 1.4 is found for the radical-like activation of propane by the ligated metal-oxide cation (phenanthroline)CuO^+ with a clear preference for the activation

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(35) A small amount of Ag_2OH^+ as a product was observed even in the absence of any reaction partner and is attributed to hydrocarbon contaminants present in the background of the high-vacuum apparatus. All data given in the text and the tables are already corrected for this background reactivity.

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Table 4. Computed Relative Energies (E_{rel} Given in eV at 0 K Relative to the Reactants) for the Reactions of Ag_2O^+ with Methane (R = CH_3), Ethane (R = C_2H_5), and Propane (R = *n*- or *i*-C_3H_7), Respectively

	R = CH_3	R = C_2H_5	R = *n*-C_3H_7	R = *i*-C_3H_7
$Ag_2O^+ + RH$	0.00	0.00	0.00	0.00
$[Ag_2O^+ \bullet RH]$	−0.55	−0.63	−0.66[a]	−0.67[a]
TS	0.08	−0.08	−0.13	−0.16
$[Ag_2OH^+ \bullet R]$	−1.38	−1.70	−1.73	−1.95
$Ag_2OH^+ + R$	−0.38	−0.58	−0.57	−0.74

[a] The encounter complexes leading to activation of primary and secondary C−H bonds have different geometries, but are only slightly different in energy (for Cartesian coordinates, see Supporting Information).

of the secondary position (k_{prim}/k_{sec} = 1:4.7 after correction for the number of hydrogen atoms in primary and secondary positions).[22b] In comparison, C−H bond activation of propane by FeO^+ occurs almost statistically and is associated with a small KIE = 1.11[40b] and also almost negligible regioselectivity in bond activation; also, activation of the various C−H bonds in *n*-butane by gaseous VO_2^+ is associated with an only moderate KIE of about 1.5.[46] According to the mechanistic insight so far gathered for the above reactions by means of theory,[22b,c,44,46,47] the moderate KIEs associated with C−H activation of alkanes by Ag_2O^+ suggest some kind of participation of the silver atoms in the bond-activation step, rather than a mere H-atom abstraction, for which lower KIEs are found.

In order to validate this qualitative conclusion derived from the consideration of the KIEs, the potential-energy surfaces for the H-atom abstractions by gaseous Ag_2O^+ from the neutral reagents methane, ethane, and propane are studied by DFT calculations (Table 4), in which we focus on the lowest-energy channels for bond activation of the reactants and release of the products according to reaction 2.

Even though the accuracy of the energetics based upon DFT should not be overestimated,[48] the results obtained agree well with the experimental findings. Thus, H-atom abstraction is predicted to be exothermic even in the case of methane, but for R = CH_3 the rate-determining transition structure (TS, E_{rel} = 0.08 eV) associated with H-atom abstraction is higher in energy than the entrance channel, and thus the reaction is predicted not to occur under thermal conditions (Figure 2). In the case of ethane, the rate-determining barrier is slightly below the entrance channel (E_{rel} = −0.08 eV), consistent with the moderate efficiency of reaction 2 experimentally observed for R = C_2H_5.

For the activation of the selectively labeled ethane CH_3CD_3 by Ag_2O^+, the barrier associated with H-atom abstraction is 0.02 eV lower than for the competing abstraction deuterium. RRKM modeling[49] of the rate constants for H- and D-atom abstractions leads to theoretical prediction of the KIE (k_H/k_D) in dependence of the internal energy available in the system (Figure 3). Although the estimation of KIE is made on a crude basis without the consideration of the rates of the backward reactions and without inclusion of possible tunneling effects, reasonably good agreement with the experimental data is achieved. Thus, for a low internal excitation of the reactants (ca. 0.2 eV), the predicted KIEs are in the range of the experimental value of 2.20 ± 0.06 eV, whereas the predicted KIEs drop to values of about 1.5 for the internal excitations larger than 1 eV.

In the case of propane, the activation barriers are even lower, as expected, but notably the TSs associated with H-atom abstraction from the primary and the secondary positions are quite similar (E_{rel} = −0.13 and −0.16 eV, ΔE_{TS} = 0.03 eV) even though formation of a 2-propyl radical as a product is energetically favored much more (ΔE_{Prod} = 0.17 eV). This result is perfectly consistent with the moderate regioselectivities of C−H bond activation derived from the labeling studies (Table 3). We further note that the TSs involve a considerable amount of reorganization of the backbone of the metal cluster (e.g., for R = CH_3, the angle α_{AgOAg} changes from 157° in the encounter complex to 137° in the TS), rather than representing mere H-atom abstraction mechanisms which matches with the conclusion derived above from the analysis of the kinetic isotope effects.

Reaction of Ag_2O^+ with Ethene. As outlined in the introduction, silver is mostly used as a catalyst for the epoxidation of ethene with molecular oxygen. While the process is applied in very large scale, it is far from being optimal, and even slight increases in the selectivity for ethylene oxide would have large economic impact.[1] Therefore, the reaction of the Ag_2O^+ cation with ethene is considered next.

$$Ag_2O^+ + C_2H_4 \rightarrow Ag_2^+ + C_2H_4O \qquad (3a)$$

$$\rightarrow Ag(C_2H_4O)^+ + Ag \qquad (3b)$$

$$Ag(C_2H_4O)^+ + C_2H_4 \rightarrow Ag(C_2H_4)^+ + C_2H_4O \qquad (4)$$

With ethene as a neutral reagent, Ag_2O^+ reacts efficiently ($k_r = 4.4 \times 10^{-10}$ cm^3 s^{-1}, ϕ = 45%) according to reactions 3a and 3b with a branching ratio of 80:20. Both reactions can be classified as O-atom transfer to the hydrocarbon substrate. The nature of the neutral C_2H_4O unit produced in reaction 3a is unknown, however; it may correspond to either acetaldehyde, vinyl alcohol, or ethylene oxide.[50] Likewise, the loss of atomic silver in reaction 3b can lead to the Ag^+ complexes of either of these C_2H_4O isomers. Formation of an intact C_2H_4O unit, rather than a metallaoxetane,[50−52] is, however, suggested by the occurrence of the secondary ion/molecule reaction 4,[53] even though also a metallaoxetane could undergo reductive elimination of a neutral C_2H_4O upon approach of another neutral reactant.[54]

Given the reasonably good coordination ability of ethene and the accessibility of several exothermic oxidation pathways, we briefly screened the other Ag_nO^+ and $Ag(AgNO_3)_n^+$ species accessible via our ESI approach (e.g., $Ag_2NO_3^+$, Ag_3O^+, Ag_3-

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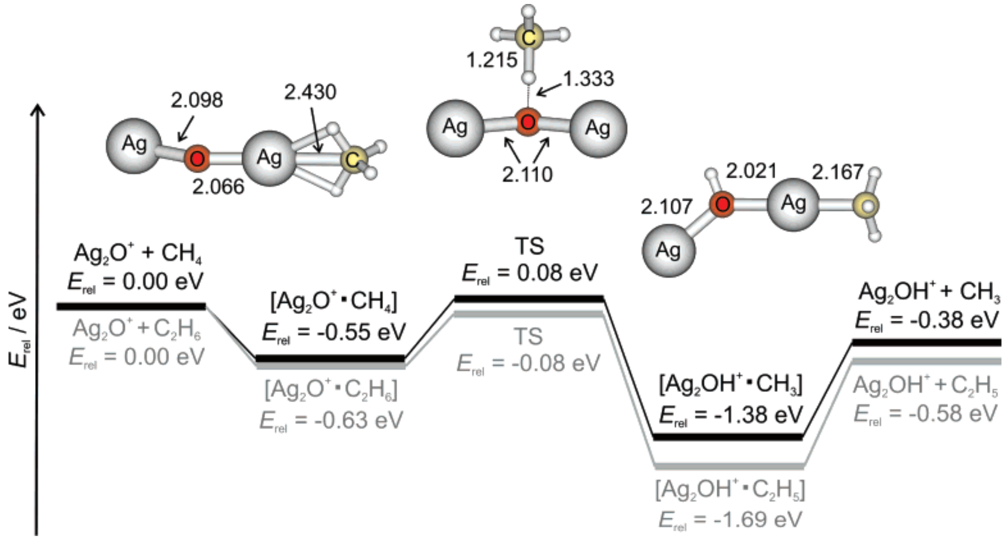

Figure 2. Calculated potential-energy profile for the H-atom abstraction from methane as well as ethane by the Ag_2O^+ cation. Relative energies given in eV and selected bond lengths are given in Å. For C−H bond activation in methane, also the computed structures are shown and selected bond lengths are given.

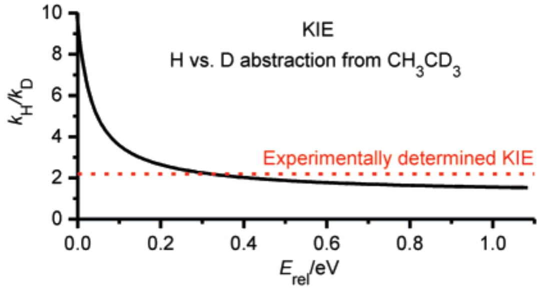

Figure 3. Calculated KIE for the H- and D-atom abstraction from CH_3-CD_3 by the Ag_2O^+ cation. The red line shows the experimentally determined KIE for this reaction. The internal energy is given in eV relative to that of the reactants $Ag_2O^+ + CH_3CD_3$.

$(NO_3)^+$, and Ag_4O^+) by means of a neutral-loss scan,[55] which demonstrated that among all ions formed upon electrospray only triatomic Ag_2O^+ permits a sufficiently efficient O-atom transfer to ethene.

Further insight into the nature of the neutral product in reaction 3a is provided by the potential-energy surface predicted by DFT calculations (Figure 4). Upon approach of ethene to the Ag_2O^+ cluster, an encounter complex $[Ag_2O^+{\cdot}C_2H_4]$ structure **1** with $E_{rel} = -1.42$ eV is formed in which the olefin is bound to one of the two silver atoms. The encounter complex can rearrange via TS **1**/**2** ($E_{rel} = -0.33$ eV) to the metallaoxetane **2** ($E_{rel} = -1.38$ eV), in which most of the spin density is located on the β-carbon atom of the oxetane. The reaction can either continue via direct O-atom transfer (TS **2**/**3**, $E_{rel} = -0.80$ eV) to afford the product complex **3** ($E_{rel} = -2.06$ eV) with an ethylene-oxide molecule bound to Ag_2^+. Dissociation of this intermediate then yields the final products Ag_2^+ and ethylene oxide ($E_{rel} = -1.03$ eV). Alternatively, O-atom transfer accompanied by hydrogen migration, TS **2**/**4** with $E_{rel} = -0.54$ eV) leads to the thermochemically preferred complex acetaldehyde/Ag_2^+ ($E_{rel} = -3.35$ eV) and finally yields $Ag_2^+ + CH_3CHO$ ($E_{rel} = -2.20$ eV). The intermediates **3** and **4** may also both lose atomic silver to afford the Ag^+ complexes of ethylene oxide and acetaldehyde, respectively. While all four pathways are energetically accessible for the reactants, the considerable energetic preference of TS **2**/**3** suggests that ethylene oxide, although thermochemically less stable, is formed as the kinetically preferred product in the gas-phase reaction.[1] Instead, formation of $Ag(C_2H_4O)^+$ in reaction 3b may be regarded as an indication for a passage via TS **2**/**4** to yield acetaldehyde bound to Ag_2^+ followed by loss of neutral Ag. In order to provide additional experimental support for the computed potential-energy surface, mass-selected Ag_2^+ was allowed to react with ethylene oxide, and as expected from Figure 4, no significant thermal reactivity was observed, whereas a putative rearrangement **3** → **4** would have allowed cluster cleavage to afford $Ag(CH_3CHO)^+ + Ag$. Further independent measurements reveal that mass-selected Ag_2O^+ reacts with ethylene oxide via H-atom abstraction to afford Ag_2OH^+ and a neutral $C_2H_3O^{\bullet}$ radical with only 12% of the gas kinetic collision rate, which is significantly slower than the primary oxidation step. In contrast, the H-atom abstraction from acetaldehyde by Ag_2O^+ occurs about 3 times faster than from ethylene oxide.

In a more general sense, the gas-phase reaction of triatomic Ag_2O^+ with ethene provides a minimal functional model for the epoxidation of ethene on silver contacts with the following key messages. (i) The metallaoxetane **2** serves as common intermediate for epoxidation and combustion, and its formation is rate-limiting.[5] (ii) In the competing routes to ethylene oxide and acetaldehyde, Ag−Ag bond formation occurs prior to closure of the three-membered ring (see TS **2**/**3**) and hydrogen migration (see TS **2**/**4**), respectively, suggesting that the lattice backbone may play a crucial role in the applied catalytic process. (iii) The potentially Lewis-acidic Ag_2^+ cation does not induce an isomerization of ethylene oxide into acetaldehyde under thermal conditions. (iv) Last, but not least, the independently investigated oxidation of ethylene oxide by Ag_2O^+ is slow compared to the initial O-atom transfer to ethene. Scheme 1 gives a sketch of the proposed scenario, which not only agrees well with the general considerations about silver-mediated

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(55) In a neutral-loss (or -gain) scan, two mass analyzers are scanned simultaneously with a fixed mass difference (Δm) while the reaction of interest is allowed to occur in between them. For ethene as a neutral reagent and $\Delta m = -16$, only those ions are detected which can transfer an oxygen atom to the substrate. Also see: ref 10a.

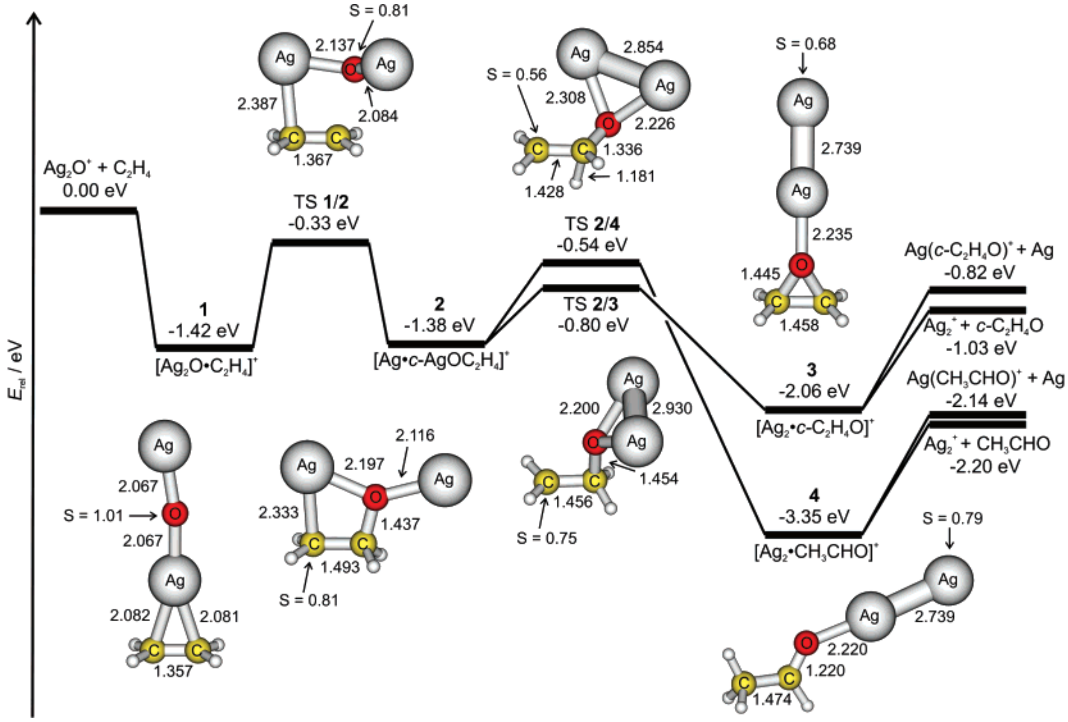

Figure 4. Potential-energy surface for O-atom transfer from Ag_2O^+ to ethene, affording either ethylene oxide or acetaldehyde (relative energies in eV). Selected bond lengths are given in Å, and also shown are the computed spin densities for those atoms at which most of it is located.

epoxidation of ethene by Stegelmann et al.[1] but is also perfectly consistent with the intermediacy of surface-metallaoxetanes as predicted and also observed by Barteau and co-workers.[5,52]

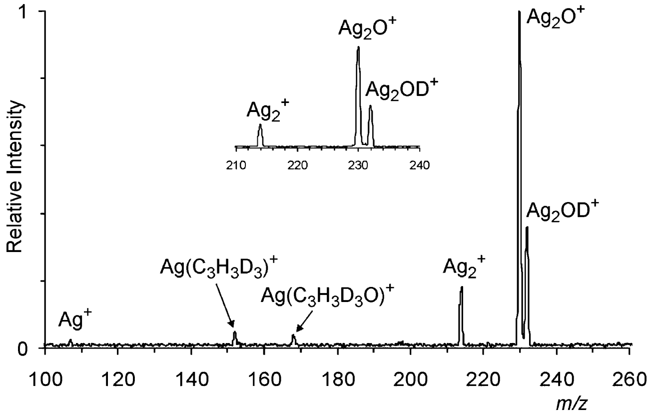

Figure 5. Reaction of mass-selected Ag_2O^+ with [3,3,3-D_3]-propene at a collision energy set nominally to 0 eV. (Inset) Separate scan of the parent-ion region at increased mass resolution. A small signal due to Ag_2OH^+ (barely visible in the figure) is due to reactions with background hydrogen-containing contaminants as verified by experiments performed with an "empty" hexapole collision cell.[35]

Reaction of Ag_2O^+ with Propene. The decisive question in the context of silver-mediated olefin epoxidation accordingly concerns the case of propene for which an efficient route using dioxygen as an oxidant still needs to be developed.[2]

$$Ag_2O^+ + CH_3CH{=}CH_2 \rightarrow Ag_2^+ + C_3H_6O \tag{5a}$$

$$\rightarrow Ag(C_3H_6O)^+ + Ag \tag{5b}$$

$$\rightarrow Ag_2OH^+ + C_3H_5^{\bullet} \tag{5c}$$

$$Ag(C_3H_6O)^+ + CH_3CH{=}CH_2 \rightarrow Ag(C_3H_6)^+ + C_3H_6O \tag{6}$$

With unlabeled propene, the primary reactions 5a−5c are observed (branching ratio 75:7 : 18, $k_r = 7.0 \times 10^{-10}$ cm^3 s^{-1}, $\phi = 70\%$). While reactions 5b and 5b are analogous to those observed for ethene, H-atom abstraction according to reaction 5c resembles the chemistry observed with the alkanes. The Ag_2O^+ cluster thus precisely mimics the problems associated with the partial oxidation of propene on silver catalysts, in which competing C−H bond activation prevents a high selectivity for epoxidation.[2] Further noteworthy is that the $Ag(C_3H_6O)^+$ species generated in reaction 5b undergoes a consecutive exchange with propene (reaction 6), which is demonstrated by the buildup of an intense $Ag(C_3H_6)^+$ signal at the expense of $Ag(C_3H_6O)^+$ at elevated propene pressure. Conceptually, reaction 6 is analogous to reaction 4 in the case of ethene and also indicates that the $Ag(C_3H_6O)^+$ ion contains an intact C_3H_6O unit. The connectivity of $Ag(C_3H_6O)^+$ is unknown, however, and several ion structures are conceivable.[53] One possibly feasible way to probe the structure of the $Ag(C_3H_6O)^+$ product is a comparison with the reactivity of independently generated of $Ag(C_3H_6O)^+$. To this end, we submitted a dilute solution of $AgNO_3$ in water/acetone (100:1) to ESI which inter alia affords an intense signal due to Ag(acetone)$^+$.[56] Upon interaction of this mass-selected $Ag(C_3H_6O)^+$ species with neutral propene, occurrence of reaction 6 is observed, which is fully consistent with a thermal reaction, given the literature values of $D(Ag^+ - \text{propene}) = 1.70 \pm 0.13$ eV[57] and $D(Ag^+ - \text{acetone}) = 1.65 \pm 0.06$ eV.[58] A conclusion about the structure of the $Ag(C_3H_6O)^+$ species

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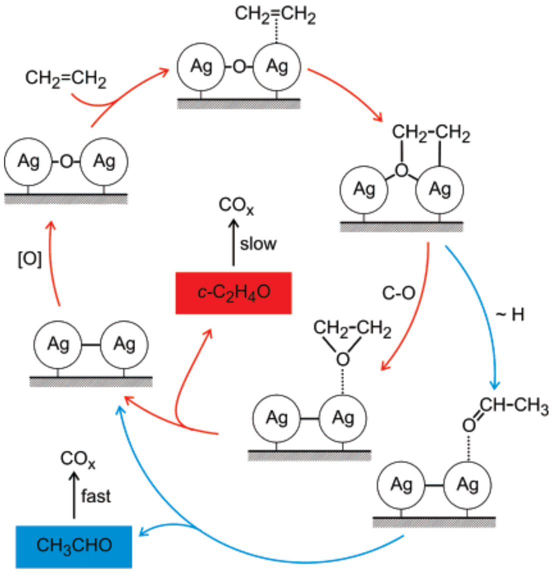
Scheme 1 Schematic Mechanistic Proposal Implied by the Present Gas-Phase Studies for Epoxidation of Ethene on Silver Surfaces



formed in reaction 5b cannot be made, however, because for Ag(propeneoxide)$^+$ as well as other isomers one might expect a similar reactivity.[53]

With [3,3,3-D_3]-propene the branching ratio of reactions 5b–5c in their deuterated variants changes to 60:11:29 and also k_r drops to 4.7×10^{-10} cm^3 s^{-1}, $\phi = 50\%$. This is consistent with the observation that exclusive D-atom transfer from $CD_3CH{=}CH_2$ to yield Ag_2OD^+ takes place (Figure 5). The altered product distribution and the lower overall rate constant can be modeled assuming a KIE of 2.0 associated with reaction 5c, which is in perfect analogy to the values obtained for the C–H bond activation of alkanes (see above). Note that this modeling does not need to involve KIEs in reactions 5b and 5b, which is consistent with the occurrence of olefin epoxidation via O-atom transfer to the double bond rather than involvement of C–H bond activation in these particular processes. Further, the Ag($C_3H_3D_3O$)$^+$ ion produced in the deuterated variant of reaction 5b undergoes a consecutive reaction with neutral $CD_3CH{=}CH_2$ in analogy to reaction 6 and is thus fully consistent with the proposed scenario.

Conclusions

In conclusion, the gas-phase reactions of Ag_2O^+ with hydrocarbons provide a simple model system for the problems encountered in the use of silver surfaces in oxidation catalysis: (i) activation of saturated hydrocarbons involves H-bond abstraction rather than O-atom transfer, (ii) epoxidation of ethene proceeds smoothly, but it is apparently associated with some amount of rearrangement leading to the more stable acetaldehyde as a product, (iii) in the case of propene the selectivity between allylic C–H bond activation and epoxidation is poor, which can be regarded as a kind of linear combination of the H-atom abstraction observed for alkanes and O-atom transfer with ethene. Note that these observations in the gas-phase reaction of Ag_2O^+ with propene nicely reflect the difficulties associated with epoxidation of propene in applied catalysis.[1,2] In addition to the mimicking of the partial oxidation of hydrocarbons on silver contacts, the present gas-phase studies, both experiment and theory, provide unique insight into the mechanisms of the oxidation reactions, thereby indirectly also offering perspectives for the further optimization of real catalysts. Due to the efficient function of alkali cations as well chlorine as promoters in silver-catalyzed olefin oxidation, one particular aim of our future studies will be the attempt to include these elements as dopants in gaseous silver-oxide clusters.[59] Given the successful application of gold catalysts for the epoxidation or propene,[2] a particular challenge for a related gas-phase experiment would be the attempt to generate a heterometallic $AgAuO^+$ species in order to probe whether the properties of both metals could be combined in the gas phase.[60]

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Supporting Information Available: Cartesian coordinates of the computed structures and complete ref 14. This material is available free of charge via the Internet at http://pubs.acs.org.

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