

# Size-Specific Reactivity of $\text{Ag}_x^+$ and $\text{Cu}_x^+$ ( $x = 1-5$ ) with Alcohols in the Gas Phase

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The gas-phase ion/molecule reactions of  $\text{Ag}_x^+$  and  $\text{Cu}_x^+$  ( $x = 1-5$ ) with  $\text{C}_1-\text{C}_4$  alcohols have been investigated using Fourier transform ion cyclotron resonance mass spectrometry. Product branching ratios and rate constants are reported for the reactions of cluster ions produced by fast atom bombardment. Dramatic differences in reactivity are seen as the number of atoms in the cluster ion is varied. Clusters with odd numbers of atoms dominate the mass spectra but are generally slower to react than clusters with even numbers of atoms. Although  $\text{Cu}^+$  and  $\text{Ag}^+$  react by dehydrogenation, dehydration, and adduct formation, the cluster ions rarely cleave bonds in the alcohols. Instead,  $\text{Ag}_x^+$  and  $\text{Cu}_x^+$  ( $x = 2, 4$ ) react by displacement of a metal atom by an alcohol molecule, indicating that these clusters contain a weakly bound metal atom. In contrast, the odd-atom clusters ( $x = 3, 5$ ) undergo slow stepwise condensation reactions with alcohols. Collision-induced dissociation is used to probe the structures of these reaction products.

## Introduction

During the past decade, the richness of gas-phase transition metal ion cluster chemistry has become evident.<sup>1</sup> An intriguing aspect of this chemistry is the dependence of reactivity on the number of atoms in the cluster. Numerous cases of size-specific effects have been reported. A striking example is  $\text{Fe}_4^+$ , which is highly reactive with ammonia<sup>2</sup> and ethylene,<sup>3</sup> although its neighboring clusters are generally unreactive or undergo only condensation reactions.  $\text{Co}_x^+$  species also exhibit size-specific reactivity, with  $\text{Co}_4^+$  reacting more rapidly with cyclohexane<sup>4</sup> and ethylene<sup>5</sup> than other small  $\text{Co}_x^+$  groups. In addition, these effects are seen for second- and third-row transition metals; for example,  $\text{Nb}_x^+$  species exhibit pronounced size-related reactivity with a variety of small molecules.<sup>6-10</sup> Even for a simple molecule such as hydrogen, the rates of chemisorption are dependent on the number of atoms in the cluster of  $\text{Nb}_x^+$ ,<sup>6</sup>  $\text{Co}_x^+$ ,<sup>11</sup> and  $\text{Fe}_x^+$ .<sup>12</sup>

Size-specific chemistry of metal clusters is often interpreted in terms of electronic effects. Theories

frequently used to explain cluster chemistry, such as the jellium<sup>13</sup> and frontier orbital<sup>14,14</sup> models, are generally based on electronic considerations without regard to geometric structures. The influence of electronic structure on cluster reactivity is illustrated by studies that correlate ionization potentials with reaction rates.<sup>12,14-16</sup> However, geometric factors are also believed to be a factor in size-specific chemistry. For example, the enhanced reactivity of  $\text{Nb}_7^+$  relative to its neighboring clusters is inconsistent with simple electrostatic models, suggesting that geometric structure is important.<sup>11,17</sup> Studies of  $\text{Co}_x^+$  and  $\text{Co}_x\text{V}_y^+$  also indicate that geometry may play a role in determining the reactivities of some small clusters.<sup>18</sup> In particular, enhanced reactivity of tetramers or pentamers has been noted for several transition-metal  $\text{M}_x^+$ .<sup>2-5,8,12,18,19</sup> Irion *et al.*<sup>2</sup> have proposed that for several transition metals  $x = 4, 5$  represents the onset of three-dimensional cluster structures that are more reactive than planar structures ( $x < 4, 5$ ).

Recently we reported that the reactions of  $\text{Ag}_x^+$  ( $x = 1-5$ ) with a variety of small hydrocarbons and oxygenated compounds show pronounced size-specific effects.<sup>20</sup> The present study expands upon this work by focusing on the reactions of  $\text{Ag}_x^+$  and  $\text{Cu}_x^+$  ( $x = 1-5$ ) with  $\text{C}_1-\text{C}_4$  alcohols. Both product formation and reaction kinetics are found to be highly dependent on the number of atoms in the cluster.

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## Experimental Section

All experiments were performed using a Bruker CMS 47X Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with an external ion source and a 4.7-T superconducting magnet.<sup>21</sup>  $\text{Cu}_x^+$  and  $\text{Ag}_x^+$  ( $x = 1-5$ ) were formed in the external source by fast atom bombardment (FAB) on targets of copper foil or pressed pellets of copper bromide or silver bromide.  $\text{Cu}_2^+$ , which was one of the most difficult ions to produce in adequate abundance for study, was produced from copper(I) chloride. A Phrasor Scientific FAB gun,<sup>22</sup> employing a 8–10-kV beam of xenon atoms and ions, was used to generate the cluster ions. The production of  $\text{Ag}_x^+$  under these conditions has been discussed previously.<sup>20</sup> For the less abundant cluster ions, such as  $\text{Ag}_4^+$  and  $\text{Cu}_4^+$ , the ability to produce these ions in yields sufficient for study was dependent on the condition of the capillaritron FAB nozzle. The hole through which bombarding ions exist the nozzle has a diameter on the order of 0.002 cm and widens with use. Metal cluster ions are produced in greatest abundance when the nozzle is new, presumably because a more tightly focused bombarding beam facilitates their formation. The timeframe over which a nozzle produced sufficient ions for study was on the order of days for  $\text{Ag}_4^+$  and hours for  $\text{Cu}_4^+$  (if at all).

Ions were transferred from the source into the FT-ICR cell by electrostatic focusing. The trapped ions were thermalized by collisions with a pulse of argon (peak pressure of ca.  $10^{-5}$  Torr) that was admitted into the analyzer vacuum chamber through a General Valve Series 9 pulsed solenoid valve. A period of 500 ms was allowed for collisional cooling<sup>23</sup> of the trapped ions and for the argon to be pumped away before monitoring ion/molecule reactions. This corresponds to 60–100 collisions of the cluster ions with argon. The ions of interest were isolated by resonant frequency ejection techniques<sup>24</sup> and allowed to react with static pressures of reactant gases. Due to the wide range of reaction rates encountered, reactant pressures were in the range  $(3-100) \times 10^{-8}$  Torr and reaction times varied from 0 to 60 s.

The primary product ion branching ratios were reproducible to  $\pm 10\%$  absolute. Rate constants, which were reproducible to  $\pm 30\%$ , were determined by observing the pseudo-first-order change in reactant ion intensity as a function of time at a constant alcohol pressure. Reported reaction efficiencies are the ratio of experimental bimolecular rate constants ( $k_{\text{obsd}}$ ) to theoretical collision rate constants, which were calculated using average dipole orientation theory<sup>25</sup> ( $k_{\text{ADO}}$ ). Pressures were measured with a calibrated ion gauge<sup>26</sup> and corrected for reactant gas ionization efficiency.<sup>27</sup> Reactions were studied to greater than 80% completion except in cases of prohibitively slow reactions. All first-order decay plots were linear, suggesting the predominance of ground-state reactant ions.

Collision-induced-dissociation (CID) experiments<sup>28</sup> were performed with static pressures of argon collision gas in the range  $(5-10) \times 10^{-7}$  Torr. The collision energy was varied from 0 to 500 eV (laboratory).

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## Results and Discussion

**Ag<sup>+</sup> Reactions.** Product ion distributions and rate constants for the primary reactions of  $\text{Ag}_x^+$  ( $x = 1-5$ ) with C<sub>1</sub>–C<sub>4</sub> alcohols are summarized in Table 1. The product ions formed during reactions of  $\text{Ag}^+$  with various small alcohols have been studied previously by Weil and Wilkins<sup>29</sup> (WW), while Jones and Staley<sup>30</sup> have investigated the secondary reactions of these species. The  $\text{Ag}^+$  reactions have been included in the present study to obtain rate constants and to provide a basis for direct comparisons between atomic metal ion and cluster ion reactivity.

$\text{Ag}^+$  is unreactive with methanol but reacts with other primary alcohols (ethanol, 1-propanol, 1-butanol, 2-methyl-1-propanol) by slow condensation to form  $\text{Ag}(\text{alcohol})^+$ . This agrees with the work of WW. In low-energy CID experiments,  $\text{Ag}(\text{alcohol})^+$  ions undergo exclusive loss of the alcohol, suggesting that  $\text{Ag}^+$  does not insert into any bonds of the alcohol. This tendency of  $\text{Ag}^+$  not to break bonds of organic ligands has also been noted for  $\text{Ag}(\text{CH}_3\text{ONO})^+$ , where  $\text{Ag}^+$  formation is the only CID process even though the  $\text{CH}_3\text{O}-\text{NO}$  bond (bond dissociation energy of 42 kcal/mol<sup>31</sup>) is extremely weak.<sup>32</sup>

For the primary alcohols, the only secondary reaction is an additional condensation step to form  $\text{Ag}(\text{alcohol})_2^+$ . While rate constants were not measured for all secondary reactions, these secondary condensations occur at rates about 10 times faster than those for the primary reactions. CID of  $\text{Ag}(\text{alcohol})_2^+$  gave successive production of  $\text{Ag}(\text{alcohol})^+$  and  $\text{Ag}^+$ , indicating two intact alcohol ligands bound to  $\text{Ag}^+$ .

Dehydrogenation dominates the reactions of  $\text{Ag}^+$  with the secondary alcohols 2-propanol and 2-butanol. These reactions are roughly 1 order of magnitude faster than the condensation reactions of primary alcohols. WW have reported similar products for the 2-propanol reactions, but primary reactions of other secondary alcohols have not been studied previously. The most thermodynamically favorable pathway involves generation of a ketone attached to the metal (reaction 1). Ketone



production from 2-propanol and 2-butanol requires 13.2 and 13.0 kcal/mol, respectively, and is a lower energy process than aldehyde production from the primary alcohols, which utilizes 16–17 kcal/mol.<sup>33</sup> Given that the bond strength of  $\text{Ag}^+-\text{H}$  is only  $16 \pm 3$  kcal/mol,<sup>34</sup> this energy requirement may be sufficient to prevent dehydrogenation of primary alcohols by  $\text{Ag}^+$ . Dehydrogenation of alcohols can produce enols; however, this process requires 5–10 kcal/mol more energy than aldehyde or ketone formation.<sup>33</sup> Enol formation was also ruled out by studying reactions with  $\text{Ag}^+$  with 2-propanol-*d*<sub>7</sub> (C<sub>3</sub>D<sub>7</sub>OH), where dehydrogenation involved

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Table 1. Primary Reactions of  $\text{Ag}_x^+$  with Small Alcohols

products and rates		rel abundance, % (rate, $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ )				
		$\text{Ag}^+$	$\text{Ag}_2^+$	$\text{Ag}_3^{+b}$	$\text{Ag}_4^+$	$\text{Ag}_5^{+b}$
methanol		NR <sup>a</sup>	NR	NR	NR	NR
	$k_{\text{obsd}}$	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>
ethanol	$\text{Ag}_{x-1}(\text{alcohol})^+ + \text{Ag}$	0	100	NR	NR	NR
	$\text{Ag}_x(\text{alcohol})^+$	100	0			
	$k_{\text{obsd}}$	$(3.9 \times 10^{-13})$	$(2.4 \times 10^{-11})$	<i>c</i>	<i>c</i>	<i>c</i>
	$k_{\text{obsd}}/k_{\text{ADO}}^d$	(0.000 27)	(0.018)			
1-propanol	$\text{Ag}_{x-1}(\text{alcohol})^+ + \text{Ag}$	0	100	0	100	0
	$\text{Ag}_x(\text{alcohol})^+$	100	0	100	0	100
	$k_{\text{obsd}}$	$(1.0 \times 10^{-11})$	$(2.2 \times 10^{-10})$	$(8.7 \times 10^{-13})$	$(5.3 \times 10^{-11})$	$(2.8 \times 10^{-12})$
	$k_{\text{obsd}}/k_{\text{ADO}}$	(0.0071)	(0.17)	(0.000 69)	(0.043)	(0.0023)
2-propanol	$\text{Ag}_{x-1}(\text{alcohol})^+ + \text{Ag}$	0	100	0	100	0
	$\text{Ag}_x(\text{ketone})^+ + \text{H}_2$	91	0	0	0	0
	$\text{Ag}_x(\text{alcohol})^+$	9	0	100	0	100
	$k_{\text{obsd}}$	$(3.7 \times 10^{-10})$	$(2.8 \times 10^{-10})$	$(1.7 \times 10^{-12})$	$(1.5 \times 10^{-10})$	$(2.5 \times 10^{-12})$
	$k_{\text{obsd}}/k_{\text{ADO}}$	(0.25)	(0.22)	(0.0014)	(0.12)	(0.0020)
1-butanol	$\text{Ag}_{x-1}(\text{alcohol})^+ + \text{Ag}$	0	100	0	100	0
	$\text{Ag}_x(\text{alcohol})^+$	100	0	100	0	100
	$k_{\text{obsd}}$	$(9.4 \times 10^{-11})$	$(3.4 \times 10^{-10})$	$(3.3 \times 10^{-12})$	$(9.9 \times 10^{-11})$	$(5.3 \times 10^{-12})$
	$k_{\text{obsd}}/k_{\text{ADO}}$	(0.065)	(0.26)	(0.0027)	(0.082)	(0.0044)
2-butanol	$\text{Ag}_{x-1}(\text{alcohol})^+ + \text{Ag}$	0	100	0	100	0
	$\text{Ag}_x(\text{ketone})^+ + \text{H}_2$	90	0	0	0	0
	$\text{Ag}_x(\text{alcohol})^+$	10	0	100	0	100
	$k_{\text{obsd}}$	$(4.9 \times 10^{-10})$	$(5.3 \times 10^{-10})$	$(8.2 \times 10^{-12})$	$(2.1 \times 10^{-10})$	$(4.5 \times 10^{-12})$
$k_{\text{obsd}}/k_{\text{ADO}}$	(0.36)	(0.41)	(0.0067)	(0.18)	(0.0038)	
2-methyl-1-propanol	$\text{Ag}_{x-1}(\text{alcohol})^+ + \text{Ag}$	0	100	0	100	0
	$\text{Ag}_x(\text{alcohol})^+$	100	0	100	0	100
	$k_{\text{obsd}}$	$(9.5 \times 10^{-11})$	$(2.7 \times 10^{-10})$	$(3.4 \times 10^{-12})$	$(9.3 \times 10^{-11})$	$(2.6 \times 10^{-12})$
	$k_{\text{obsd}}/k_{\text{ADO}}$	(0.066)	(0.21)	(0.0028)	(0.078)	(0.0022)
2-methyl-2-propanol	$\text{Ag}_{x-1}(\text{alcohol})^+ + \text{Ag}$	0	100	0	100	0
	$\text{Ag}_x(\text{alkene})^+ + \text{H}_2\text{O}$	100	0	0	0	0
	$\text{Ag}_x(\text{alcohol})^+$	0	0	100	0	100
	$k_{\text{obsd}}$	$(4.6 \times 10^{-10})$	$(4.2 \times 10^{-10})$	$(8.8 \times 10^{-12})$	$(2.5 \times 10^{-10})$	$(7.0 \times 10^{-12})$
	$k_{\text{obsd}}/k_{\text{ADO}}$	(0.32)	(0.33)	(0.0071)	(0.24)	(0.0059)

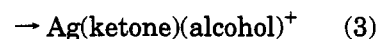
<sup>a</sup> NR indicates that no reaction was observed. <sup>b</sup> The  $\text{Ag}_3^+$  and  $\text{Ag}_5^+$  reactions are pressure-dependent adduct formation. The reported rate constants are the average of several values obtained at pressures of  $(4-7) \times 10^{-7}$  Torr. <sup>c</sup> The lack of reaction at alcohol pressures on the order of  $10^{-6}$  Torr for reaction times of at least 5 s indicates that  $k_{\text{obsd}} < 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . <sup>d</sup> Reaction efficiency.

exclusive loss of the alcohol hydrogen. In addition, the reaction of  $\text{Ag}^+$  with 2-propanol- $d_8$  was investigated and a small kinetic isotope effect was observed,  $k_{\text{H}}/k_{\text{D}} = 1.24 \pm 0.05$ . This is consistent with the rate-determining step involving cleavage of a C–H(D) or O–H(D) bond.

The CID of  $\text{Ag}(\text{ketone})^+$  yields only  $\text{Ag}^+$ , again suggesting no  $\text{Ag}^+$  insertion into bonds of the ligand. Detailed mechanistic studies were not performed on this system; however, WW studied the dehydrogenation of  $\text{CD}_3\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{CH}_2\text{OD}$  by  $\text{Au}^+$  and proposed a mechanism involving metal ion "insertion" into the C–H bond  $\alpha$  to the oxygen followed by an  $\alpha$ -hydride shift from OH(D). A similar mechanism presumably occurs for dehydrogenation involving  $\text{Ag}^+$ . This is consistent with our observation of HD loss during the reaction of  $(\text{CD}_3)_2\text{CDOH}$ . Given that  $\text{Ag}^+$  (and  $\text{Cu}^+$ ) is a  $d^{10}$  species, it is likely that  $\text{Ag}^+$  does not actually oxidatively insert into the C–H bond. Instead, this bond cleavage may entail an intermediate similar to that proposed by Armentrout and co-workers<sup>35</sup> for the reactions with  $\text{Cu}^+$  and alkanes; this process involves a three-center–two-electron bond with the electrons in the bond to be cleaved being donated into the empty 4s orbital of  $\text{Cu}^+$ . Dissociative attachment or ion/dipole mechanisms, which involve dissociation following metal ion coordination to organic molecules, is also possible and has, for example, been

proposed for the reactions of  $\text{Cu}^+$  with nitriles,<sup>36</sup> esters, and ketones.<sup>37</sup>

The  $\text{Ag}(\text{ketone})^+$  primary products react further with the alcohol by ligand displacement (reaction 2) and condensation (reaction 3). This agrees with the work of WW but is in contrast to the results of Jones and Staley,<sup>30</sup> where secondary dehydrogenation reactions were observed.



The tertiary alcohol 2-methyl-2-propanol has no  $\alpha$ -hydrogens available for the dehydrogenation process. Instead, the only primary reaction product is  $\text{Ag}(\text{C}_4\text{H}_9)^+$ , which is also the major product observed by WW. CID on  $\text{Ag}(\text{C}_4\text{H}_9)^+$  yields only  $\text{Ag}^+$ . Secondary reactions involve ligand displacement and condensation (reactions 2 and 3). This also conflicts with Jones and Staley's<sup>30</sup> observation of secondary dehydration reactions.

In general,  $\text{Ag}^+$  is relatively unreactive with small alcohols. One reason is its  $4d^{10}$  electronic configuration;

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Table 2. Primary Reactions of  $\text{Cu}_x^+$  with Small Alcohols

	products and rates	rel abundance, % (rate, $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ )			
		$\text{Cu}^+$	$\text{Cu}_2^+$	$\text{Cu}_3^{+b}$	$\text{Cu}_5^{+b}$
methanol	$\text{Cu}_{x-1}(\text{alcohol})^+ + \text{Cu}$	0	100	0	NR <sup>a</sup>
	$\text{Cu}_x(\text{alcohol})^+$	100	0	100	
	$k_{\text{obsd}}$	$(1.6 \times 10^{-12})$	$(8.1 \times 10^{-10})$	$(3.3 \times 10^{-13})$	c
	$k_{\text{obsd}}/k_{\text{ADO}}^d$	(0.000 98)	(0.57)	(0.000 23)	
ethanol	$\text{Cu}_{x-1}(\text{alcohol})^+ + \text{Cu}$	0	100	0	NR
	$\text{Cu}_x(\text{aldehyde})^+ + \text{H}_2$	100	0	0	
	$\text{Cu}_x(\text{alcohol})^+$	0	0	100	
	$k_{\text{obsd}}$	$(5.8 \times 10^{-10})$	$(8.1 \times 10^{-10})$	$(4.5 \times 10^{-12})$	c
	$k_{\text{obsd}}/k_{\text{ADO}}$	(0.36)	(0.56)	(0.0033)	
1-propanol	$\text{Cu}_{x-1}(\text{alcohol})^+ + \text{Cu}$	0	100	0	0
	$\text{Cu}_x(\text{H}_2\text{O})^+ + \text{alkene}$	29	0	0	0
	$\text{Cu}_x(\text{alkene})^+ + \text{H}_2\text{O}$	29	0	0	0
	$\text{Cu}_x(\text{aldehyde})^+ + \text{H}_2$	38	0	0	0
	$\text{Cu}_x(\text{alcohol})^+$	4	0	100	100
	$k_{\text{obsd}}$	$(6.3 \times 10^{-10})$	$(1.0 \times 10^{-9})$	$(2.9 \times 10^{-11})$	$(3.1 \times 10^{-11})$
	$k_{\text{obsd}}/k_{\text{ADO}}$	(0.39)	(0.74)	(0.022)	(0.024)
2-propanol	$\text{Cu}_{x-1}(\text{ketone})^+ + \text{H}_2 + \text{Cu}$	0	9	0	0
	$\text{Cu}_{x-1}(\text{alcohol})^+ + \text{Cu}$	0	91	0	0
	$\text{Cu}_x(\text{H}_2\text{O})^+ + \text{alkene}$	48	0	0	0
	$\text{Cu}_x(\text{alkene})^+ + \text{H}_2\text{O}$	25	0	0	0
	$\text{Cu}_x(\text{ketone})^+ + \text{H}_2$	8	0	0	0
	$\text{Cu}_x(\text{alcohol})^+$	19	0	100	100
	$k_{\text{obsd}}$	$(9.7 \times 10^{-10})$	$(1.0 \times 10^{-9})$	$(5.2 \times 10^{-11})$	$(6.3 \times 10^{-11})$
	$k_{\text{obsd}}/k_{\text{ADO}}$	(0.60)	(0.72)	(0.039)	(0.050)
1-butanol	$\text{Cu}_{x-1}(\text{alkene})^+ + \text{H}_2\text{O} + \text{Cu}$	0	8	0	0
	$\text{Cu}_{x-1}(\text{aldehyde})^+ + \text{H}_2 + \text{Cu}$	0	10	0	0
	$\text{Cu}_{x-1}(\text{alcohol})^+ + \text{Cu}$	0	82	0	0
	$\text{Cu}_x(\text{H}_2\text{O})^+ + \text{alkene}$	41	0	0	0
	$\text{Cu}_x(\text{alkene})^+ + \text{H}_2\text{O}$	25	0	0	0
	$\text{Cu}_x(\text{aldehyde})^+ + \text{H}_2$	18	0	0	0
	$\text{Cu}_x(\text{alcohol})^+$	16	0	100	100
	$k_{\text{obsd}}$	$(7.3 \times 10^{-10})$	$(1.3 \times 10^{-9})$	$(1.1 \times 10^{-10})$	$(7.9 \times 10^{-11})$
	$k_{\text{obsd}}/k_{\text{ADO}}$	(0.45)	(0.90)	(0.084)	(0.064)
2-butanol	$\text{Cu}_{x-1}(\text{alkene})^+ + \text{H}_2\text{O} + \text{Cu}$	0	16	0	0
	$\text{Cu}_{x-1}(\text{alcohol})^+ + \text{Cu}$	0	84	0	0
	$\text{Cu}_x(\text{H}_2\text{O})^+ + \text{alkene}$	53	0	0	0
	$\text{Cu}_x(\text{alkene})^+ + \text{H}_2\text{O}$	28	0	0	0
	$\text{Cu}_x(\text{ketone})^+ + \text{H}_2$	5	0	0	0
	$\text{Cu}_x(\text{alcohol})^+$	14	0	100	100
	$k_{\text{obsd}}$	$(1.1 \times 10^{-9})$	$(1.2 \times 10^{-9})$	$(1.1 \times 10^{-10})$	$(8.8 \times 10^{-11})$
	$k_{\text{obsd}}/k_{\text{ADO}}$	(0.65)	(0.85)	(0.086)	(0.071)
2-methyl-1-propanol	$\text{Cu}_{x-1}(\text{alkene})^+ + \text{H}_2\text{O} + \text{Cu}$	0	12	0	0
	$\text{Cu}_{x-1}(\text{alcohol})^+ + \text{Cu}$	0	88	0	0
	$\text{Cu}_x(\text{H}_2\text{O})^+ + \text{alkene}$	36	0	0	0
	$\text{Cu}_x(\text{alkene})^+ + \text{H}_2\text{O}$	54	0	0	0
	$\text{Cu}_x(\text{alcohol})^+$	10	0	100	100
	$k_{\text{obsd}}$	$(1.3 \times 10^{-9})$	$(1.3 \times 10^{-9})$	$(1.2 \times 10^{-10})$	$(5.1 \times 10^{-11})$
	$k_{\text{obsd}}/k_{\text{ADO}}$	(0.81)	(0.93)	(0.089)	(0.041)
2-methyl-2-propanol	$\text{C}_4\text{H}_9^+ + \text{Cu}_x\text{OH}^+$	7	0	0	0
	$\text{Cu}_{x-1}(\text{alkene})^+ + \text{H}_2\text{O} + \text{Cu}$	0	27	0	0
	$\text{Cu}_{x-1}(\text{alcohol})^+ + \text{Cu}$	0	73	0	0
	$\text{Cu}_x(\text{H}_2\text{O})^+ + \text{alkene}$	41	0	0	0
	$\text{Cu}_x(\text{alkene})^+ + \text{H}_2\text{O}$	47	0	0	0
	$\text{Cu}_x(\text{alcohol})^+$	5	0	100	100
	$k_{\text{obsd}}$	$(7.6 \times 10^{-10})$	$(1.2 \times 10^{-9})$	$(7.8 \times 10^{-11})$	$(1.4 \times 10^{-10})$
	$k_{\text{obsd}}/k_{\text{ADO}}$	(0.46)	(0.89)	(0.059)	(0.11)

<sup>a</sup> NR indicates that no reaction was observed. <sup>b</sup> The  $\text{Cu}_3^+$  and  $\text{Cu}_5^+$  reactions are pressure-dependent adduct formation. The reported rate constants are the average of several values obtained at pressure of  $(4-7) \times 10^{-7}$  Torr. <sup>c</sup> The lack of reaction at alcohol pressures on the order of  $10^{-6}$  Torr for reaction times of at least 5 s indicates that  $k_{\text{obsd}} < 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . <sup>d</sup> Reaction efficiency.

transition metals such as  $\text{Fe}^+$ ,<sup>38-40</sup>  $\text{Co}^+$ ,<sup>38,41</sup>  $\text{Ni}^+$ ,<sup>38,39</sup>  $\text{Cr}^+$ ,  $\text{Mo}^+$ ,<sup>40</sup> and  $\text{Rh}^+$ ,<sup>42</sup> which have only partially filled d orbitals, are much more reactive.

**$\text{Cu}^+$  Reactions.** As the rate constant and product

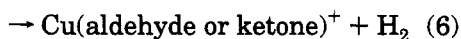
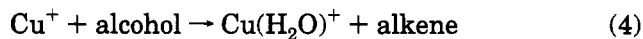
ion data in Table 2 indicate,  $\text{Cu}^+$  is much more reactive with alcohols than  $\text{Ag}^+$ . This may be related to the fact that, during the initial stages of interaction, the smaller  $\text{Cu}^+$  gets closer to the alcohol than the larger  $\text{Ag}^+$ . Thermodynamic data support stronger bonding with  $\text{Cu}^+$  because  $D(\text{Ag}^+-\text{H}) = 16 \pm 3 \text{ kcal/mol}^{34}$  is weaker than  $D(\text{Cu}^+-\text{H}) = 22.1 \pm 3 \text{ kcal/mol}^{43}$  (although both  $\text{M}^+-\text{H}$  bonds are very weak relative to those of other

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transition metals). While  $D(Ag^+-CH_3)$  is not known,  $Cu^+$  has the weakest metal ion-methyl bond in the first-row transition series ( $D(Cu^+-CH_3) = 29.7 \pm 1.7$  kcal/mol<sup>35</sup>).<sup>44</sup> On the basis of the  $M^+-H$  bond energies, the  $Ag^+-CH_3$  bond is anticipated to be extremely weak.

Condensation, which dominated the  $Ag^+$  reactions, occurs to a more limited extent for  $Cu^+$ . Instead, dehydration (reactions 4 and 5) and dehydrogenation (reaction 6) are the major processes. These same path-



ways were observed by WW,<sup>29</sup> whose study also included reactions of  $Cu^+$  and several small alcohols. The most notable difference in the results of the two studies is that for the dehydration process we observe primarily alkene elimination (reaction 4), while WW found predominantly water loss (reaction 5). This may be a function of the reaction times chosen in assigning primary product ratios. (Both studies involved comparable pressures around  $10^{-8}$ – $10^{-7}$  Torr.) Our work indicates that secondary reactions of  $Cu(H_2O)^+$  with the alcohol proceed more rapidly than reactions of  $Cu(\text{alkene})^+$  or  $Cu(\text{aldehyde or ketone})^+$ .  $Cu(H_2O)^+$  reacts by ligand displacement to produce  $Cu(\text{alcohol})^+$ ; WW generally reported  $Cu(\text{alcohol})^+$  in greater abundance as a primary product than the present study indicates. Therefore, it is possible that WW obtained primary product ratios at a time after some secondary reactions, which progress at near the collision rate, had occurred. Our own reported primary abundances of  $Cu(\text{alcohol})^+$  may be slightly high for the same reason.

Dehydration reactions 4 and 5 probably proceed by a process similar (but not identical) to the established mechanism of Allison and Ridge,<sup>38</sup> which was first proposed for the reactions of  $Fe^+$ ,  $Co^+$ , and  $Ni^+$  with alcohols. This involves metal ion addition to the C–O bond followed by a  $\beta$ -hydrogen shift and reductive elimination of various stable neutrals. As noted above for  $Ag^+$ , it is likely that the  $d^{10}$   $Cu^+$  does not actually oxidatively insert into the C–O bond but instead forms an intermediate which utilizes the empty 4s orbital of  $Cu^+$ . WW have performed reactions with  $Au^+$  and deuterium-labeled ethanols to confirm that the water loss involves the alcohol hydrogen and the  $\beta$ -hydrogen.<sup>29</sup> Our own reactions of  $Cu^+$  with  $(CD_3)_2CDOH$  reveal exclusive loss of the alcohol hydrogen during both dehydration and dehydrogenation. It is also possible that C–H bond activation, similar to the mechanisms proposed by Schwarz and co-workers<sup>39</sup> for the reactions of  $Fe^+$ ,  $Co^+$ , and  $Ni^+$  with propanol, is involved in these reactions, particularly for the larger alcohols. In an effort to gain additional mechanistic information, we investigated the reactions of  $Cu^+$  with 2-propanol- $d_8$ . No kinetic isotope effect ( $k_H/k_D = 0.99 \pm 0.04$ ) was found, suggesting that the cleavage of a C–H(D) or O–H(D) bond does not occur in a rate-determining step. However, because the elimination of  $H_2$  is a minor primary process (8% of the products), it is possible that this

pathway involves a small isotope effect that we were unable to observe. Product ion abundances showed only a slight isotope effect, with the deuterated reagent giving an decrease in  $Cu(H_2O)^+$  by about 8% (to account for ca. 40% of the products), while the relative abundances of  $Cu(C_3H_6)^+$  and  $Cu(C_3H_6O)^+$  both increased slightly.

Dehydrogenation reaction 6 should involve a mechanism similar to the one discussed above for  $Ag^+$  and  $Au^+$ . In contrast to the  $Ag^+$  reaction that involved only  $Ag(\text{ketone})^+$  formation,  $Cu^+$  dehydrogenates both linear and branched alcohols, producing ketone and aldehyde products, respectively.  $Cu^+$  does not dehydrogenate methanol, which may indicate that reaction 6 is endothermic for methanol. Around 22 kcal/mol is required to produce formaldehyde from methanol, while only 16–17 kcal/mol is utilized in the production of aldehydes from other small primary alcohols.<sup>33</sup>

All  $Cu^+$  primary product ions react readily with the neutral alcohol. While some dehydration occurs, by far the dominant secondary pathway is ligand displacement to produce  $Cu(\text{alcohol})^+$ . These reactions are all facile but, as noted above,  $Cu(H_2O)^+$  reacts the fastest. For example, the rate constant for the reaction of  $Cu(H_2O)^+$  with 2-methyl-2-propanol is  $1.2 \times 10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, while  $Cu(C_4H_8)^+$  has a corresponding rate constant of  $9.2 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. In analogy to the  $Ag^+$  reactions,  $Cu(\text{alcohol})^+$  species produced in these secondary reactions condense with a second alcohol molecule to form  $Cu(\text{alcohol})_2^+$  as the terminal product.

Low-energy CID of  $Cu(\text{alcohol})^+$  and  $Cu(\text{alcohol})_2^+$  shows abundant loss of the intact alcohol. In addition, dehydrogenation and dehydration are also minor CID pathways. In general, formation of  $Cu(\text{alkene})^+$  and  $Cu(\text{aldehyde})^+$  or  $Cu(\text{ketone})^+$  occurs at slightly lower collision energies than for  $Cu(H_2O)^+$ . This is in contrast with the  $Ag^+$  study, where only alcohol loss occurs, but is consistent with the enhanced primary reactivity of  $Cu^+$  relative to  $Ag^+$ .

**$Ag_2^+$  and  $Cu_2^+$  Reactions.** Many diatomic cluster ions are less reactive than their corresponding atomic metal ions.<sup>4,45,46</sup> However, with regard to kinetics, that is not true for the reactions of  $Ag_2^+$  and  $Cu_2^+$  with small alcohols. For  $C_2$ – $C_4$  alcohols, displacement of a metal atom by the alcohol (reaction 7;  $M = Ag, Cu$ ) is a major



reaction pathway. In fact, that is the only process observed for  $Ag_2^+$ . For  $Cu_2^+$ , reaction 7 is the most abundant primary pathway, but some  $Cu(\text{alkene})^+$  and  $Cu(\text{ketone})^+$  or  $Cu(\text{aldehyde})^+$  also appear as minor products. In addition, for both dimers, low levels of dissociation to produce  $M^+$  were occasionally observed. This process is very dependent on experimental conditions, and ejection sequences were set up carefully to avoid inadvertent kinetic excitation of ions which, for  $Cu_2^+$ , can induce  $Cu^+$  formation and also lead to dissociation of  $Cu(\text{alcohol})^+$ .

The primary products formed from  $Ag_2^+$  and  $Cu_2^+$  undergo secondary reactions and CID in an identical manner to the corresponding product ions generated from  $Ag^+$  and  $Cu^+$ . This indicates, for example, that

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$M(\text{alcohol})_{1,2}^+$  species produced from  $M^+$  and from  $M_2^+$  have the same structures.

The dimer ions generally react faster than the corresponding atomic metal ions. While ethanol is slow to react with  $\text{Ag}_2^+$ , the other alcohols react with efficiencies ( $k_{\text{obsd}}/k_{\text{ADO}}$ ) in the range of 0.17–0.41. 2-Propanol, 2-butanol, and 2-methyl-2-propanol, the three alcohols which react most readily with  $\text{Ag}^+$ , react at virtually the same rate with both  $\text{Ag}_2^+$  and  $\text{Ag}^+$ . For  $\text{Cu}_2^+$ , methanol reacts readily while the corresponding  $\text{Cu}^+$  reaction is extremely slow. The other alcohols react slightly faster with  $\text{Cu}_2^+$  (efficiencies of 0.56–0.93) than with  $\text{Cu}^+$  (efficiencies of 0.36–0.81), with the  $\text{Cu}_2^+$  reactions having the highest rate constants measured in this study. There is a general trend toward increasing reaction rates as the number of carbons in the alcohol increases. This may result from increasing reaction exothermicity and is consistent with the order of  $\text{Ag}^+$  affinities to alcohols being  $\text{C}_4 > \text{C}_3 > \text{C}_2 > \text{C}_1$ , which has been reported by McLuckey *et al.*<sup>47</sup>

The dominance of metal–metal bond cleavage in the  $\text{Ag}_2^+$  and  $\text{Cu}_2^+$  reactions indicates weak bonding in the dimers. CID experiments confirm this, with both dimers dissociating to produce  $M^+$  under extremely low energy conditions. In addition, Cheeseman and Eyer<sup>48</sup> have recently used charge-transfer reactions to obtain ionization potentials for various Cu, Ag, and Au clusters. Their results yield values of  $D(\text{Ag}^+-\text{Ag}) = 38.0 \pm 5.1$  kcal/mol and  $D(\text{Cu}^+-\text{Cu}) = 46.8 \pm 3.5$  kcal/mol.<sup>48</sup> In addition, Weisshaar and co-workers have obtained a value of  $D(\text{Cu}^+-\text{Cu}) = 42.4 \pm 1.8$  kcal/mol by resonant two-photon ionization-photoelectron spectroscopy.<sup>49</sup> These are among the lowest known bond energies for transition metal dimer ions.<sup>33,50</sup>

The facile exothermic displacement of Ag and Cu by  $\text{C}_3$  and  $\text{C}_4$  alcohols suggests that for  $\text{Ag}_2^+$  and  $\text{Cu}_2^+$ , once a reaction intermediate has formed, the charge in the complex primarily resides on one metal atom while the other metal atom is essentially acting as a ligand. This displacement indicates that  $D[M^+(\text{alcohol})]$  is greater than  $D(M^+-M)$  and sets lower limits of  $D[\text{Ag}^+(\text{alcohol})] > 38.0$  kcal/mol and  $D[\text{Cu}^+(\text{alcohol})] > 42.4$  kcal/mol. The slow reaction of ethanol with  $\text{Ag}^+$  may mean that this reaction is near thermoneutral, placing  $D[\text{Ag}^+(\text{ethanol})]$  within a few kcal/mol of  $D(\text{Ag}^+-\text{Ag})$ . This is on the same order as  $D[\text{Ag}^+(\text{C}_2\text{H}_4)]$ , which is reported as  $33.7 \pm 1.5$  kcal/mol.<sup>51</sup> Likewise, the slow reaction of  $\text{Cu}^+$  and methanol may indicate that  $D[\text{Cu}^+(\text{methanol})]$  is near  $D(\text{Cu}^+-\text{Cu})$ . This is consistent with the literature value of  $D[\text{Cu}^+(\text{H}_2\text{O})]^+ = 37.5 \pm 1.0$  kcal/mol.<sup>52</sup> During their ionization potential experiments, Cheeseman and Eyer<sup>48</sup> found that several aromatic amines used as charge-transfer reagents also reacted with the dimer ions via metal atom displacement.

The reactions of  $\text{Cu}_2^+$  with 2-propanol and the butanols are the only cluster ion reactions in this study

that yield products involving organic bond cleavage. Here, dehydrogenation or dehydration of the alcohols is seen in conjunction with loss of a Cu atom. The sequence of these eliminations relative to  $\text{Cu}^+-\text{Cu}$  bond cleavage is unclear. The  $\text{Cu}(\text{alkene})^+$ ,  $\text{Cu}(\text{aldehyde})^+$ , or  $\text{Cu}(\text{ketone})^+$  species formed are generally the lowest energy CID products of the corresponding  $\text{Cu}(\text{alcohol})^+$ . Therefore, Cu atom displacement may occur first, with the resulting  $\text{Cu}(\text{alcohol})^+$  retaining sufficient internal energy to undergo neutral elimination. The possibility also exists that loss of Cu and  $\text{H}_2$  or  $\text{H}_2\text{O}$  is occurring simultaneously, producing  $\text{Cu}(\text{H}_2)$  or  $\text{Cu}(\text{H}_2\text{O})$  as the eliminated neutral species and involving a mechanism in which both metal atoms are active participants in coordination to the alcohol. To gain mechanistic information, reactions were performed with 2-propanol- $d_8$ . No kinetic isotope effect was observed ( $k_{\text{H}}/k_{\text{D}} = 1.01 \pm 0.06$ ), providing inconclusive evidence on the sequences of these processes. If initial Cu atom displacement were occurring, this displacement might be the rate-determining step and result in no kinetic isotope effect. Unfortunately, a kinetic isotope effect was not found for the reactions of  $\text{Cu}^+$  with 2-propanol ( $k_{\text{H}}/k_{\text{D}} = 0.99 \pm 0.04$ ). Therefore, since  $\text{Cu}^+$  can break alcohol bonds without an observed isotope effect, the possibility also exists that alcohol bond cleavage by  $\text{Cu}_2^+$  is unaffected by hydrogen isotope composition.

**$\text{Ag}_3^+$  and  $\text{Cu}_3^+$  Reactions.** Under our experimental conditions,  $\text{Ag}_3^+$  is the most abundant cluster ion produced from FAB on silver metal, silver halides, and silver oxides.<sup>20</sup> CID studies have also noted the exceptional stability of  $\text{Ag}_3^+$ .<sup>20,53</sup> In the present study, these same observations are true for  $\text{Cu}_3^+$ . In addition,  $\text{Ag}_x^+$  and  $\text{Cu}_x^+$  species with odd  $x$  have even numbers of electrons; this should result in spin pairing and enhanced stability relative to even- $x$  clusters.<sup>54</sup> Katakuse *et al.*<sup>55</sup> have also used a one-electron shell model with valence electrons bound in a square-well-like potential to explain the high stability of  $\text{Ag}_3^+$  and  $\text{Cu}_3^+$ , which are considered to be “magic number” clusters.

This high stability is evident in the reactions of  $\text{Ag}_3^+$  and  $\text{Cu}_3^+$  with alcohols. Slow sequential addition of three molecules is observed, producing  $M_3(\text{alcohol})_3^+$  as the terminal product. In addition,  $M_3(\text{C}_4\text{H}_9\text{OH})_2(\text{C}_4\text{H}_8)^+$  formed as a minor product during tertiary reactions involving the butanols; these ions then react to produce  $M_3(\text{C}_4\text{H}_9\text{OH})_3(\text{C}_4\text{H}_8)^+$ . This is similar to the tertiary reaction of  $\text{Ag}_3^+$  and 2-butylamine, which Buckner *et al.*<sup>53</sup> found to produce  $\text{Ag}_3(\text{C}_4\text{H}_9\text{NH}_2)_2(\text{C}_4\text{H}_6)^+$  by deamination and dehydrogenation of the amine. Our previous study of  $\text{Ag}_3^+$  indicated that  $\text{Ag}_3(\text{ligand})_3^+$  is also the terminal product in the reactions of  $\text{Ag}_3^+$  with various alkenes,<sup>20</sup> while Freas and Campana<sup>56</sup> have shown that  $\text{Cu}_3(\text{C}_4\text{H}_{10})_3^+$  is a terminal product in the reactions of  $\text{Cu}_x^+$  ( $x = 1-5$ ) with 2-methylpropane.

$\text{Ag}_3^+$  and  $\text{Cu}_3^+$  are far slower to react with alcohols than the corresponding  $M^+$  and  $M_2^+$ . The measured reaction efficiencies for  $\text{Ag}_3^+$  indicate that, at most, 1 collision out of every 100 results in a condensation reaction. Reaction rates are generally a factor of 10

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**Table 3. Pressure Dependence on the Reaction of  $\text{Ag}_3^+$  with 2-Propanol**

2-propanol press, $10^{-7}$ Torr	av time between collisions, ms <sup>a</sup>	$k_{\text{obsd}}$ , $\text{cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>	$k_{\text{obsd}}/k_{\text{ADO}}$
1.0	250	$8.8 \times 10^{-13}$	0.000 70
3.0	84	$1.2 \times 10^{-12}$	0.000 93
6.0	42	$1.8 \times 10^{-12}$	0.001 4
9.2	27	$2.4 \times 10^{-12}$	0.001 9

<sup>a</sup> Calculated using average dipole orientation theory.<sup>25</sup>

higher for  $\text{Cu}_3^+$  but are still extremely low. In addition, rate constants reported in Tables 1 and 2 for the trimer ions were measured at pressures in the range  $(4-7) \times 10^{-7}$  Torr. At pressures below *ca.*  $1 \times 10^{-7}$  Torr, these reactions were not observed. This is not the case for the  $\text{M}^+$  and  $\text{M}_2^+$  reactions (except for the extremely slow  $\text{Ag}^+$ /ethanol and  $\text{Cu}^+$ /methanol reactions), which proceed at pressures in the low  $10^{-8}$  Torr range. Table 3 provides representative data on this pressure dependence obtained from the reactions of  $\text{Ag}_3^+$  with 2-propanol. In general, a pressure increase by a factor of 10 in this region results in a factor of 3 increase in the rate of condensation. These data clearly indicate that collisional stabilization, which has been observed in many cases involving adduct formation,<sup>57-59</sup> is necessary to produce  $\text{M}_3(\text{alcohol})^+$ .

Secondary and tertiary reactions to produce  $\text{M}_3(\text{alcohol})_2^+$  and  $\text{M}_3(\text{alcohol})_3^+$  are also very slow with rates of the same order of magnitude as the primary reactions. Collisional stabilization again impacts these condensation reactions. CID of selected  $\text{M}_3(\text{alcohol})_{1-3}^+$  species revealed sequential alcohol elimination, indicating that three distinct ligands are bound to  $\text{M}_3^+$  and that metal insertion into bonds of the alcohol has not occurred. No additional ligand attachment to  $\text{M}_3(\text{alcohol})_3^+$  was found, even under "severe" conditions such as reaction times of 60 s at alcohol pressures of  $10^{-6}$  Torr. Under similar conditions,  $\text{Ag}^+$  and  $\text{Cu}^+$  attached only two alcohols.

$\text{Ag}_3$  and  $\text{Cu}_3$  neutral clusters have been studied extensively by theoretical<sup>60</sup> and spectroscopic<sup>61,62</sup> methods. A triangular structure is often proposed. For example, electron spin resonance spectroscopy studies have suggested an isosceles triangular structure for  $\text{Ag}_3$ .<sup>62</sup> While such studies have been much less common for cations, *ab initio* theoretical studies have also predicted that  $\text{Ag}_3^+$  and  $\text{Cu}_3^+$  exist in a highly stable triangular geometry.<sup>63,64</sup> Our experimental observations do not provide definitive structural information; however, the formation of a terminal  $\text{M}_3(\text{alcohol})_3^+$  ion is consistent with a triangular structure where one alcohol molecule attaches to each metal atom.

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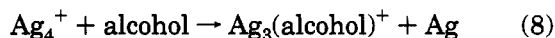
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**$\text{Ag}_4^+$  and  $\text{Cu}_4^+$  Reactions.** Under our experimental conditions,  $\text{Ag}_4^+$  and  $\text{Cu}_4^+$  are formed in much lower abundance than species with  $x = 1-3, 5$ .<sup>20</sup> Low tetramer ion yields have also occurred under other bombardment conditions employed to produce  $\text{Ag}_x^+$  and  $\text{Cu}_x^+$ .<sup>48,53,55,65-67</sup> Previously, we found that  $\text{Ag}_4^+$  dissociates at extremely low CID energies to produce  $\text{Ag}_3^+$ ;<sup>20</sup> this suggests a weak  $\text{Ag}_3^+-\text{Ag}$  bond. Our attempts to produce sufficient  $\text{Cu}_4^+$  to investigate its CID or reactions have been unsuccessful. Evidently, much of the  $\text{Ag}_4^+$  and  $\text{Cu}_4^+$  that is originally produced by FAB dissociates or charge transfers immediately following ion formation. In particular, the longer (millisecond) time scales of FT-ICR studies<sup>20,53,67</sup> allows increased time for cluster ions to undergo metastable decomposition following ion formation; thus, in comparison to quadrupole and sector mass spectrometer studies,<sup>65,66</sup> FT-ICR experiments show decreased relative intensities of less stable species such as  $\text{Ag}_4^+$  and  $\text{Cu}_4^+$ .

The reactions of  $\text{Ag}_4^+$  with alcohols also support weak bonding of the fourth Ag in the cluster. Silver atom displacement (reaction 8) is the major process involving the alcohol. Some dissociation of the cluster to produce



$\text{Ag}_3^+$  occurs and is difficult to control or quantify due to the extremely low intensities of the reactant ion. Reaction efficiencies are relatively low (0.043-0.24), but these reactions occur even at pressures in the  $10^{-8}$  Torr region.  $\text{Ag}_3(\text{alcohol})^+$  is produced by silver atom displacement from  $\text{Ag}_4^+$  significantly faster than it is produced by condensation reactions of  $\text{Ag}_3^+$ . The observation of reaction 8 for  $\text{C}_3$  and  $\text{C}_4$  alcohols indicates that  $D[\text{Ag}_3^+(\text{alcohol})] > D[\text{Ag}_3^+-\text{Ag}]$ .

Our unsuccessful attempts to generate  $\text{Cu}_4^+$  have involved FAB ionization of various copper oxides, copper halides, copper foil, and copper powder. A previous FT-ICR study involving particle bombardment of copper with a 20-kV  $\text{Xe}^+$  beam has also noted the complete absence of  $\text{Cu}_4^+$  from the resulting mass spectra.<sup>68</sup> In addition,  $\text{Cu}_4^+$  does not form by direct laser desorption of copper metal in an FT-ICR.<sup>67</sup> In the present work,  $\text{Cu}_4^+$  was produced in sufficient quantity for study on only one fleeting occasion. In this instance,  $\text{Cu}_4^+$  reacted with 2-propanol by Cu atom displacement to generate  $\text{Cu}_3(2\text{-propanol})^+$ . The measured rate constant was  $5.0 \times 10^{-10}$   $\text{cm}^2$  molecule<sup>-1</sup> s<sup>-1</sup>, which was not reproduced due to loss of the  $\text{Cu}_4^+$  signal. This value and the corresponding reaction efficiency of 0.40 indicate that  $\text{Cu}_4^+$  reaction with 2-propanol is significantly faster than the corresponding  $\text{Ag}_4^+$  reaction (efficiency 0.13). This limited observation suggests that  $\text{Cu}_4^+$  reacts with alcohols by metal atom displacement, in a manner analogous to that for  $\text{Ag}_4^+$ , with  $\text{Cu}_4^+$  reactions proceeding at faster rates than the  $\text{Ag}_4^+$  reactions. This is consistent with our results for the other  $\text{Ag}_x^+$  and  $\text{Cu}_x^+$  species ( $x = 1-3, 5$ ).

**$\text{Ag}_5^+$  and  $\text{Cu}_5^+$  Reactions.** Adduct formation to generate  $\text{M}_5(\text{alcohol})^+$  is the only primary process for

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$\text{Ag}_5^+$  and  $\text{Cu}_5^+$ . These reactions occur at virtually the same rates as the corresponding  $\text{Ag}_3^+$  and  $\text{Cu}_3^+$  condensation reactions. Also, in analogy to the  $\text{M}_3^+$  chemistry, the rate constants for  $\text{M}_5^+$  were measured at pressures in the range  $(4-7) \times 10^{-7}$  Torr. Essentially no reaction occurs at lower pressures, indicating that collisional stabilization is needed to observe adduct formation.

The  $\text{M}_5(\text{alcohol})^+$  ions also undergo condensation reactions.  $\text{Cu}_5^+$  sequentially adds three alcohols, producing  $\text{Cu}_5(\text{alcohol})_3^+$ , with the first two additions occurring at approximately the same rate and the third being slower. Evidence of extremely slow formation of  $\text{Cu}_5(2\text{-methyl-2-propanol})_4^+$  was seen, but attachment of four ligands was not observed with the other alcohols. In contrast,  $\text{Ag}_5^+$  produced  $\text{Ag}_5(\text{alcohol})_2^+$  as the major terminal product found in our studies. However, given the slowness of these reactions and the low initial ion intensities of  $\text{Ag}_5^+$  and  $\text{Cu}_5^+$ , we cannot rule out the formation of additional products which we were unable to observe. The only observation of additional ligand attachment was again for 2-methyl-2-propanol, with the third condensation step proceeding at a much lower rate than the first two steps. For both pentamers, loss of  $\text{H}_2\text{O}$  is a minor secondary or tertiary pathway for some alcohols. Due to the low initial ion yields of  $\text{Ag}_5^+$  and  $\text{Cu}_5^+$ , CID studies were not performed on the products of these reactions.

The FAB spectra of silver and copper metals and halide salts show odd-atom clusters in much greater abundance than even-atom clusters.  $\text{Ag}_5^+$  and  $\text{Cu}_5^+$  do not form in the abundances seen for the "magic"  $\text{M}_3^+$  but are generated in much higher yields than  $\text{M}_4^+$ . Both  $\text{M}_5^+$  clusters produce  $\text{M}_3^+$  as the lowest energy CID product. While this could imply that an intact  $\text{M}_2$  has been lost, the ease of dissociation of  $\text{M}_4^+$  (to produce

$\text{M}_3^+$ ) means that sequential elimination of two metal atoms from  $\text{M}_5^+$  cannot be ruled out.

### Conclusions

Silver and copper cluster ions  $\text{Ag}_x^+$  and  $\text{Cu}_x^+$  ( $x = 1-5$ ) exhibit pronounced size-specific chemistry in their gas-phase reactions with  $\text{C}_1-\text{C}_4$  alcohols. Dehydrogenation, dehydration, and adduct formation are major processes in the reactions of  $\text{Ag}^+$  and  $\text{Cu}^+$ . In terms of both product formation and reaction kinetics,  $\text{Cu}^+$  is more reactive than  $\text{Ag}^+$ . These atomic metal ions have  $d^{10}$  electronic configurations and weak  $\text{M}^+-\text{H}$  and  $\text{M}^+-\text{CH}_3$  bonds, which render them generally less reactive than other transition metal ions. The chemistry of  $\text{Ag}_2^+$  and  $\text{Cu}_2^+$  is dominated by weak  $\text{M}^+-\text{M}$  bonds that are readily cleaved to yield  $\text{M}(\text{alcohol})^+$ . These results are most consistent with, following formation of the reaction intermediate, one metal atom acting as the charge size while the second metal atom behaves as a weakly bound ligand. In contrast, the trimer ions undergo very slow condensation reactions to form  $\text{M}_3(\text{alcohol})_3^+$ . The ion/molecule reactions, along with ion production and dissociation results, support a stable triangular structure for  $\text{Ag}_3^+$  and  $\text{Cu}_3^+$ .  $\text{Ag}_4^+$  reacts much more readily than  $\text{Ag}_3^+$ , with silver atom displacement as the major primary process. ( $\text{Cu}_4^+$  was not produced in adequate quantities for study by FAB/FT-ICR.) The pentamer ions revert to slow condensation reactions, with  $\text{Ag}_5(\text{alcohol})_2^+$  and  $\text{Cu}_5(\text{alcohol})_3^+$  observed as the predominant terminal products.

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