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Rates of Hydride Abstraction from Amines via Reactions with Ground-State Ag^+ and Cu^+

S. W. Sigsworth and A. W. Castleman, Jr.*

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received June 3, 1988*

Abstract: Rates of reaction of ground-state Ag^+ and Cu^+ with mono- (MMA), di- (DMA), and trimethylamine (TMA) were measured. In all cases except Ag^+ with monomethylamine the reactions were found to be fast bimolecular ones. The values are 2.1, 1.7, and 1.5×10^{-9} cm^3 s^{-1} for Cu^+ with MMA, DMA, and TMA, respectively, and 1.6 and 1.4×10^{-9} cm^3 s^{-1} for Ag^+ with DMA and TMA, respectively. The products for the reactions are the amine ions with a hydrogen atom removed. The bimolecular channel for the reaction of Ag^+ with MMA is endothermic, and an association complex is found to be the product of the reaction. The observed rates are found to be in reasonably good accord with the predictions of a parametrized trajectory calculational method.

Elucidating the properties and reactivity of amines has formed the basis for a number of studies over the years. Recently, the importance of mono-, di-, and trimethylamine (MMA, DMA, and TMA, respectively) has been "brought to light" concerning the role of these methylated ammonia analogues in the global nitrogen cycle.[1] Several groups have studied the reactivity and measured the rate coefficients for bimolecular reactions of molecular amine ions and of the hydride-abstracted amine ions,[2,3] and the termolecular reactivity of protonated amines has also been studied extensively.[3–6] Su and Bowers[7] investigated rates of proton transfer from aliphatic ions to various amines. In terms of properties, proton affinity, ionization potential, and hydrogen affinity values have been determined for various amines including NH_3, MMA, DMA, and TMA.[8] Additionally, appearance potentials of various hydride-abstracted amine ions have been measured, and their common structural features have been discussed.[9–14] Radecki and Allison[13] observed evidence of insertion and β-hydrogen shift mechanisms for the reactions of Co^+ with various amines. They found that in general Co^+ apparently inserts into N–H bonds, as well as into C–C and C–N bonds of secondary and tertiary amines. The failure to insert into the C–N bond of primary amines has been attributed to energetics stemming from the weakness of the Co–N bond that would be formed. Babinec and Allison[15] were able to qualitatively correlate the reactivity of metal ions with electronic configuration by observing the reactions of all the monopositive metal ions from Cr^+ to Zn^+ with a primary amine, *n*-propylamine. Thus far, to the best of the author's knowledge, there have been no quantitative studies of reaction rates for ground-state metal ions with amines.

In the present study, reaction rates of hydride abstraction from DMA and TMA were determined for ground-state Cu^+ and Ag^+ and for MMA with Cu^+; the thermodynamic properties preclude hydride abstraction from MMA in the case of Ag^+.[14] The results and their implications to the reaction mechanisms are discussed herein.

Experimental Section

Rate coefficients were measured in a flow reactor at ambient room temperature (ca. 298 K). The apparatus and technique have been described previously.[16] This apparatus consists of a flow tube having a length of 1 m and an inside diameter of 7.2 cm. Thermionic emission is used to produce metal ions in their ground state; the ions are carried downstream by a flow of helium introduced at a mass flow rate of 10 000 sccm. Amine molecules are introduced 74 cm upstream from the sampling orifice and allowed to react with the metal ions. A small portion of the gas is sampled into the detection region, while the bulk of the gas is pumped away by a fast roots pump, which maintains the flow-tube pressure at a desired value between 0.2 and 1.3 Torr. The reaction in the sampled mixture is essentially quenched due to the low pressures produced via differential pumping from 650- and 300-L/s diffusion pumps. The ions are focused, mass filtered with a quadrupole, and detected by means of a channeltron and pulse-counting techniques.

As heretofore, the ion velocity, V_p, is determined by perturbing the ion distribution in the flow tube via electric pulsing at two points in the flow tube and monitoring the signal of the metal ion as a function of time with a multichannel analyzer. The necessary data consist of the ion velocity, flow-tube pressure, reaction distance (constant), ambient temperature, the reactant ion (Ag^+ or Cu^+) intensity as a function of amine mixture mass flow rate, and the concentration of the amine mixture. Because all of the reactions considered here are fast, it was necessary to dilute the amine reactants (typically 2% amine in helium). Adsorption–desorption posed a problem in the flow tube, and it was typically found necessary to run 5–8 sccm of the 2% amine mixture for up to 15 min to "condition" the flow tube. Until this was done, successive 40-s signal scans of the reactant ion would demonstrate drift in intensity at a single mass flow rate of the amine mixture.

The natural abundances of copper atoms are 69% ^{63}Cu and 31% ^{65}Cu. Generally, the more abundant isotope at *m/z* 63 was monitored in these experiments. However, $^{65}Cu^+$ was monitored in the corresponding monomethylamine (MMA) reaction because a tertiary product of this reaction, $(MMA)_2H^+$, occurs at the same *m/z* as $^{63}Cu^+$. Briefly, Cu^+ abstracts a hydride unit from MMA (MW = 31 amu), leaving an ion at *m/z* 30, which transfers a proton to another MMA molecule (see rest of text) to form protonated MMA at *m/z* 32. This species than adds MMA to form an ion at *m/z* 63 (protonated MMA dimer).

As before,[16] the natural logarithm of the reactant ion intensity is in each case plotted versus the number density of amine (see Figure 1) as the reactions are all conducted under pseudo-first-order conditions (concentration reactant ion $\ll$ concentration of reactant neutral). The negative slope of this linear plot is multiplied by the ion velocity and divided by the reaction distance to give the second-order rate coefficient. The pressure was varied to see whether the rate coefficients were truly second order or if they had a pressure dependence. A plot of the pressure dependence of three of the abstraction reactions is shown in Figure 2. Only the case of Ag^+ with MMA showed dependence on pressure for the effective bimolecular rate coefficient (see Figure 3).

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Table I. Reactions of Metal Cations with Methyl-Substituted Amines

reaction	pressure range, Torr	rate coeff[a] $k^{(2)}$, 10^{-9} cm^3 s^{-1}
(1) $Cu^+ + (CH_3)_3N \rightarrow H_2C{=}N(CH_3)_2^+ + CuH$	0.34–0.71	1.5
(2) $Ag^+ + (CH_3)_3N \rightarrow H_2C{=}N(CH_3)_2^+ + AgH$	0.39–0.75	1.4
(3) $Cu^+ + (CH_3)_2NH \rightarrow H_2C{=}NH(CH_3)^+ + CuH$	0.46–0.72	1.7
(4) $Ag^+ + (CH_3)_2NH \rightarrow H_2C{=}NH(CH_3)^+ + AgH$	0.34–0.71	1.6
(5) $Cu^+ + CH_3NH_2 \rightarrow H_2C{=}NH_2^+ + CuH$	0.23–0.89	2.1
(6) $Ag^+ + CH_3NH_2 + He \rightarrow Ag^{\bullet+}CH_3NH_2 + He$	0.27–1.32	*b*

[a] Error estimated to be ±10%. [b] Transition regime termolecular kinetics.

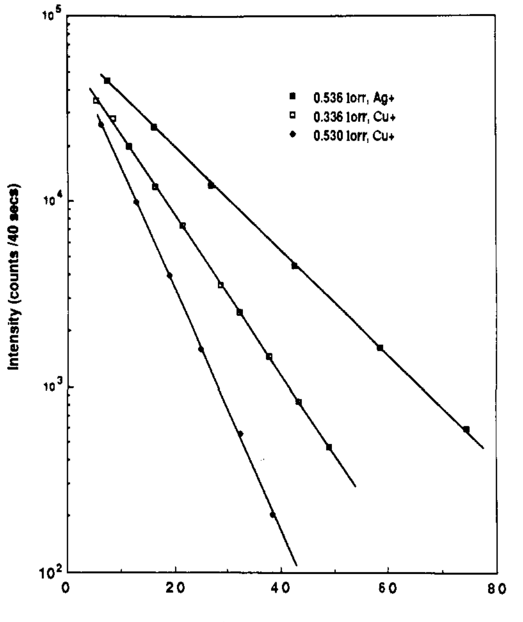

Figure 1. Metal ion intensity vs number density MMA. The data for Ag^+ and Cu^+ at 0.5 Torr clearly show that Cu^+ reacts faster. Note that for the Cu^+ data the slope is steeper at 0.5 Torr than at 0.3 Torr. The carrier gas flow rate is held constant while the pumping speed is varied to give slower ion velocities, V_p, and larger reaction times at higher pressures. Thus the slope changes with pressure even though the rate coefficient is constant for Cu^+ with MMA.

The amines were all standard lecture bottle gases, and the helium was passed through liquid nitrogen cooled sieves to eliminate problems due to water interference.

Results and Discussion

Rate coefficients were measured for Cu^+ and Ag^+ reacting with methyl-substituted amines. In general the reaction products are the metal hydride and an ion consisting of an amine molecule containing one less hydride unit

$$M^+ + (CH_3)_nNH_{3-n} \rightarrow (CH_3)_{n-1}NH_{3-n}{=}CH_2^+ + MH \qquad n = 1\text{–}3 \quad (1)$$

where M represents a metal atom. A listing of the reactions studied, the ion products, the pressure range investigated, and the measured rate constants are given in Table I. The respective metal hydride neutrals are inferred from the energetics[14] of the reaction and are not directly identified in the experiments. Relative to the other isomeric possibilities, the quaternary immonium structure given for the $C_nH_{2n+2}N^+$ product ions in Table I and in eq 1 is thought to be quite stable.[10]

All the reactions, except one, are fast bimolecular reactions with rates varying from 2.1 × 10^{-9} cm^3 s^{-1} for Cu^+/MMA to 1.4 × 10^{-9} cm^3 s^{-1} for Ag^+/TMA. These deduced rate coefficients are found to be pressure independent. The exception is the reaction of Ag^+ with MMA, which is determined to be endothermic for the abstraction channel. In this case an ion–ligand association reaction complex is identified as the product. Under the conditions of the experiment, the reaction of Ag^+ with MMA was determined to be a termolecular reaction in the transition pressure regime situated between the low-pressure termolecular and high-pressure saturated termolecular kinetic regimes (see Figure 3). Since the effective termolecular coefficients asymptotically increase with decreasing third-body number density (or pressure) to the true low-pressure termolecular rate coefficient, a lower limit can be determined. For Ag^+/MMA this lower limit is 6.9 × 10^{-26} cm^6 s^{-1}. This reaction follows a termolecular pathway because the bimolecular channel is thermodynamically inaccessible.[14] For the case of termolecular reactions in the low-pressure regime the effective bimolecular rate coefficient varies directly with the third-body number density or pressure. It is interesting to note

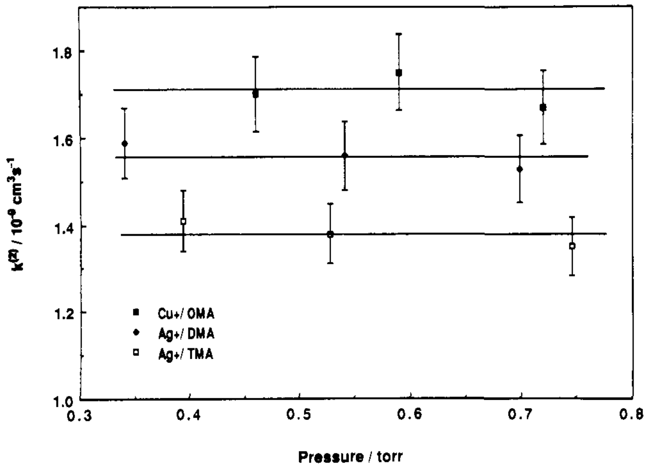

Figure 2. Pressure dependence of the binary rate coefficients for three hydride-abstraction reactions. The data points have ±5% error bars with horizontal lines drawn at the average value (to three significant digits) of the rate coefficients for the reaction pairs Cu^+/DMA, Ag^+/DMA, and Ag^+/TMA, respectively. Note that Ag^+ reacts slower than Cu^+ and that TMA reacts slower than DMA.

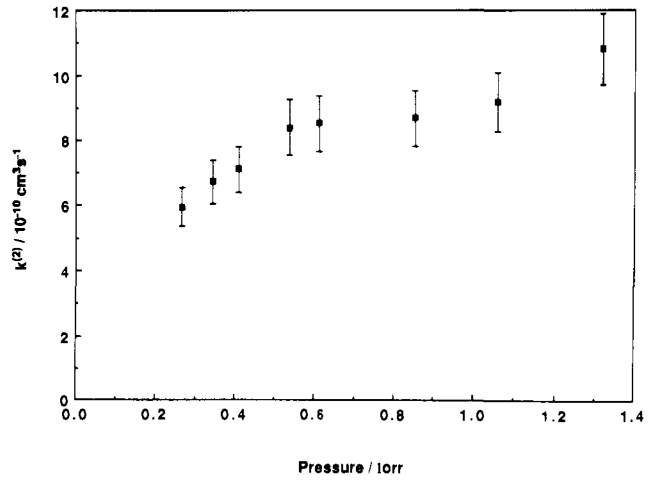

Figure 3. Dependence upon pressure of the effective binary rate coefficients for the condensation reaction of Ag^+ with MMA. This is a case of a termolecular reaction in the transition pressure regime. The data are shown with ±10% error bars. In the high-pressure or saturated regime the data *would* show no pressure dependence while for the low-pressure regime (perhaps ≤0.25 Torr) the $k^{(2)}$ values *would* be directly proportional to pressure at a given temperature.

Table II. Comparison of Properties of Reactants and the Experimental and Theoretical Rates of Reaction

			reactant ion rate coeff $k^{(2)}$, 10^{-9} cm^3 s^{-1}			
			Cu^+		Ag^+	
reactant molecule	$\alpha \times 10^{25}$ cm^3	μ_D, D	expt	theory	expt	theory
MMA	40.1[a]	1.31[b]	2.1	1.7	*c*	1.6
DMA	58.6[a]	1.03[b]	1.7	1.5	1.6	1.4
TMA	77.1[a]	0.612[b]	1.5	1.3	1.4	1.2

[a] See ref 7. LeFevre, R. J. W. *Adv. Phys. Org. Chem.* **1965**, *3*, 1. [b] Nelson, R. D., Jr.; Lide, D. R., Jr.; Maryott, A. A. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1966**, *10*. [c] Transition regime kinetics, $k^{(3)} \geq 6.9 \times 10^{-26}$ cm^6 s^{-1} from largest effective termolecular coefficient. Product is adduct of reactants.

that, for the bimolecular or abstraction reactions, the Ag^+ rate coefficients are each about 90% of the value of the corresponding Cu^+ rate coefficients. If the bimolecular channel was thermodynamically accessible, it would be reasonable to expect a value of about 1.9×10^{-9} cm^3 s^{-1} for Ag^+ with CH_3NH_2. The highest measured *effective* bimolecular coefficient for this reaction pair is 1.1×10^{-9} cm^3 s^{-1}.

It is informative to consider the magnitudes of the measured bimolecular reaction rates in terms of the polarizabilities and the dipole moments of mono-, di-, and trimethylamine; the values are listed in Table II. Also listed in the table are the measured reaction rates and the theoretically predicted values deduced using the parametrized trajectory calculations[17] of Su and Chesnavich. As can be seen from the table, the polarizability increases with methyl substitution while the dipole moment decreases. These factors offset each other somewhat as large values of each of these parameters favor faster reactions, but the dipole moment effect predominates as might be expected. The dipole moments of the methyl amines and the reaction rates both decrease with increasing methyl substitution.

Calculations using the Su and Chesnavich method[17] yield rate coefficients that are about 90% of the value of the experimentally determined coefficients reported here. It is also of interest to note that, not only when comparing Ag^+ experimental values with Cu^+ values but also when comparing the theoretical values of the two ions, the bimolecular reaction rate coefficients of Ag^+ are each about 90% of the corresponding Cu^+ rate coefficients; see Table II.

It is quite clear that the above bimolecular reactions are all single-collision reactions. This follows from the fact that the reactions are independent of pressure and that the metal ions disappear via reaction at a rate corresponding to the rate at which collisions occur. If a collision complex is formed, the lifetime of this complex relative to products is much shorter than the lifetime relative to reactants, such that redissociation to reactants does not occur. The measured rate coefficients are for the rate of disappearance of the metal ion and are expected to reflect the rate of appearance of products (in this case, an amine less one hydride unit and the metal hydride). Both association to form a stabilized adduct and hydride abstraction were observed to be fast reactions in these experiments. However, whenever the abstraction reaction is thermodynamically allowed it always dominates and for these cases the metal ion–amine adducts or stabilized clusters constituted only 3% or less of the total product distribution. As the reaction rates have an estimated error of 10%, this source of uncertainty should not have a very noticeable effect on the reaction rate.

The reactions in question may be represented by the expression

$$M^+ + AH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (M^+AH)^* \xrightarrow{k_2} A^+ + MH \qquad (2)$$

(where M represents a metal atom and AH an amine molecule) for which the overall rate of reaction is just

$$\frac{-d[M^+]}{dt} = \frac{k_1 k_2 [M^+][AH]}{k_{-1} + k_2} \qquad (3)$$

if one considers that a steady-state condition exists for $[MAH^+]^*$. We see that M^+ and AH form $[MAH^+]^*$ at the rate $k_1[M^+][AH]$, which corresponds to a rate less than or equal to the rate at which M^+ and AH collide. Noting that the experimental rate of M^+ disappearance corresponds to the collisional rate, we conclude that $k_{-1} \ll k_2$, which allows $k_1 k_1/(k_{-1} + k_2)$ to approach its greatest value, k_1. The steady-state approximation, together with the concept that $k_{-1} \ll k_2$, implies that $k_1[M^+][AH] = k_2[MAH^+]^*$ or that, as expected, the overall reaction rate is the rate of disappearance of reactants.

The technique used to produce the metal ions, thermionic emission, is a surface ionization technique. Elkind and Armentrout[18] point out that, in general, surface ionization produces mainly ground-state ions, although ions in low-lying excited states may also be present. Excited states are not considered to be a problem in the flow tube due to multiple collisions with the buffer gas, which tend to quench[19] these states to the ground level. Moreover, the lowest lying excited state for Ag^+ and Cu^+ is the $^3D_3$ state at 4.86 eV above the ground $^1S_0$ state for Ag^+ and 2.72 eV above the ground-state for Cu^+.[20] Clearly, for the temperatures of the flow tube and even at the filament, a negligible amount of even the first excited state will be present. For example, at a filament temperature of 2000 K, at most 10^{-5}% of the Cu^+ ions are excited (even less for Ag^+).

Ground-state Ag^+ and Cu^+ have d^{10} configurations and are left with an empty s orbital with which they can bond; it is therefore conceivable that ligands could bond by donating two electrons to this empty orbital. Thus, one might expect the nitrogen lone pair of NH_3 or of methylamines to be the initial site for metal ion–ligand interaction (see first step in eq 6). As evident from the discussion of the influence of polarizabilities and dipole moments in connection with Su and Chesnavich calculations,[17] for the magnitudes of the values in the systems being considered, changes in the dipole moment have a proportionally greater effect on the reaction rate than do similar changes in the polarizability. This suggests that lone pairs that are oriented in the direction of the dipole vector would preferentially be the site of attack of the metal ion rather than a methyl hydrogen, around which an attractive electron density may be induced. In view of the fast reaction rates, this may imply that the neutral molecule rapidly reorients with respect to the ion during the collision.

It does not appear that Ag^+ and Cu^+ directly insert into bonds. Insertion involves the formation of two bonds in a manner that would seem to require having two orbitals on the metal ion with one electron in each. This arrangement is ideal for inserting the metal ion between the two entities originally bonded together. As the original bond homolytically divides, the bond electrons can pair up with the two unpaired electrons on the metal ion. This is applicable to excited-state Cu^+ and Ag^+ but not their ground states. For Cu^+ (and Ag^+) the lowest energy excited state, a triplet state $^3D_3$, has an unpaired electron in each of a 3d and the 4s orbital (4d and 5s for Ag^+). Thus, this excited state seems ideal for the formation of two bonds by direct insertion. However, as Babinec and Allison[15] have pointed out, promotion to this state from the ground state is thermodynamically unfeasible for reaction with organics. In the present case, 2.72 eV is required for excitation of Cu^+ to the $^3D_3$ state, while 4.86 eV is required for promotion of Ag^+; the present reactions are exothermic by less than 1.4 eV.[14,21]

Freiser et al.[22] have studied the reactions of Cu^+ with various esters and ketones. They explained their results as dissociative attachment, whereby the Cu^+ becomes associated to the electron-rich oxygen units of the molecules, a mechanism which is

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(17) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

(18) Elkind, J. L.; Armentrout, P. B. *J. Phys. Chem.* **1986**, *90*, 5736.

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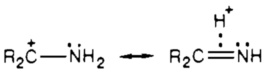
(20) Radzig, A. A.; Smirnov, B. M. *Reference Data on Atoms, Molecules and Ions*; Springer-Verlag: Berlin, 1985.

(21) From ref 14, the pertinent energies for the reactions are as follows: Cu^+/DMA, Cu^+/TMA, ≤1.4 eV exothermic; Cu^+/MMA, Ag^+/DMA, Ag^+/TMA, ≤0.7 eV exothermic; Ag^+/MMA, endothermic.

(22) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641.

followed by an intramolecular hydrogen migration and then dissociation of the resulting species. Radecki and Allison[13] reported that Co^+ abstracts a hydride unit from amines to form CoH whenever there is an α-hydrogen available but not when there is no α-hydrogen. This is explained as metal ion attack at the α-hydrogen, association of the resulting metal hydride to the α-carbon, followed by elimination of the neutral metal hydride. The protonated imine structure (shown here for the case of a primary amine reactant)



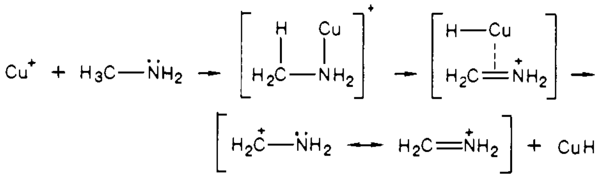
$$R_2\overset{+}{C}-\dot{N}H_2 \longleftrightarrow R_2C\overset{\overset{H^+}{\vdots}}{=}\dot{N}H \qquad (4)$$

proposed by Radecki and Allison[13] as a product of the hydride abstraction is supposed to be stable, but Loudon and Webb[9] proposed a slightly different structure, also thought to be quite stable,[10] for which the lone pair of the nitrogen is used in forming a double bond to the α-carbon

$$R_2\overset{+}{C}-\ddot{N}H_2 \leftrightarrow R_2C{=}\overset{+}{N}H_2 \qquad (5)$$

The actual structure is unknown.[13]

The ions Cu^+ and Ag^+ may abstract hydrogen according to the mechanism proposed for the analogous reaction of Co^+ with amines (note: in general, hydrogen abstraction was just one of several product channels for the reactions of Co^+ [13]). However, it is not unreasonable to consider that initial attack occurs at the lone pair of the nitrogen followed by rearrangement and elimination steps analogous to the ideas suggested[22] to account for Cu^+ reactions with esters and ketones. After initial dative coordination of the amine unit to the metal ion, one can envision how the hydride abstraction might occur. Counting the nitrogen atom as the α-position, there is the possibility of β-hydride shift followed by elimination of the neutral metal hydride from the complex (illustrated here for Cu^+ and methylamine):



(6)

Ground-state Cu^+ and Ag^+ are known to be biligand coordinate.[23,24] These are strong ligand coordinations to the metal ion thought to be facilitated by spd hybridization of the metal ion orbitals. Thus, Cu^+ and Ag^+ can readily coordinate to two entities as required by the mechanism in eq 6.

For the reaction of Cu^+ with methylamine or CH_3NH_2, the CH_4N^+ product ion was observed in the present study to react with another CH_3NH_2 molecule to produce a protonated amine. Similarly, we found that $C_2H_6N^+$ from $(CH_3)_2NH$ reacts with another $(CH_3)_2NH$ molecule to form protonated DMA. However, $C_3H_8N^+$ from TMA does not react with TMA to give a protonated amine. Our findings are consistent with observations previously reported by Jones and Harrison[2] and Munson.[3] Munson interpreted these findings to mean that the amine molecule presumably gains a proton from the $(M - 1)^+$ ion (where $M - 1$ represents an amine molecule less one hydrogen unit) directly by proton transfer of a nitrogen-bound hydrogen to the neutral amine. This could occur through a hydrogen bond type interaction for the case of $H_2C{=}NH_2^+$ or by direct proton transfer in the case of a protonated imine. This reaction occurs rapidly on the order of the collision rate of 10^{-9} cm^3 s^{-1} (reported values range from 0.7×10^{-9} cm^3 s^{-1} for Munson[3] to 2.4×10^{-9} cm^3 s^{-1} for Jones and Harrison[2]).

Summary

In the present study rates for hydride abstraction from the methyl-substituted amines (MMA, DMA, and TMA) via reaction with Ag^+ and Cu^+ were found to correspond to the rate of collision of reactants in all cases except for Ag^+ with MMA. Thermodynamic considerations preclude the occurrence of the abstraction in this case and a stabilized collision complex is the product observed.

In accord with predictions derived from results of the parameterized trajectory calculations of Su and Chesnavich,[17] the Ag^+ abstraction rate coefficients are each about 90% of the corresponding Cu^+ values.

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