MLCT state is higher in energy than remote. For all other complexes eq 6 is employed. For all 423-type complexes, the DQ^{2+} 2+/1+ reduction potential is −0.65 V, as shown in Table I. Once values of ΔG are known, estimation of k_{et} follows easily, using eq 11, with $C = -104$ mV, and $b = -2022$ mV. Estimates presented in this Appendix are listed in Table III.

$(Ru(bpy)_2(42n\text{-}DQ^{2+}))^{4+}$ Series. The onset of emission in the complex $Ru(bpy)_2(DMB)^{2+}$ is 2.20 eV (Table IV), and the Ru 3+/2+ potential for $Ru(bpy)_2(423\text{-}DQ^{2+})$ is +1.24 V (Table I). Equation 7 thus yields a value of 1.24 − 2.20 = −0.96 V for the Ru 2+*/3+ potential in $Ru(bpy)_2(423\text{-}DQ^{2+})$. With values of −0.65 V for the DQ^{2+} 2+/1+ potential, and 0.05 V (50 mV) for E_{AR}, eq 8 yields an estimate of ΔG equal to −0.96 + 0.65 − 0.05 = −0.36 V or −360 mV. For $Ru(bpy)_2(422\text{-}DQ^{2+})$ and $Ru(bpy)_2(424\text{-}DQ^{2+})$, DQ^{2+} 2+/1+ potentials (Table I) are −0.44 and −0.77 V, respectively, yielding respective ΔG estimates (Table III) of −240 and −570 mV. For these complexes, k_{et} values are estimated as $k_f(\text{obsd})/\alpha(\text{calcd})$, ($\alpha = 0.064$). These k_{et}^{-1} estimates are found in Table III.

$(Ru(DMB)_2(423\text{-}DQ^{2+}))^{4+}$. The onset of emission in the complex $Ru(DMB)_3^{2+}$ (2.19 eV, Table IV) and the Ru 3+/2+ potential (+1.13 V, Table I) are combined using eq 7, to yield a value of 1.13 − 2.19 = −1.06 V for the Ru 2+*/3+ potential. With the DQ^{2+} 2+/1+ potential equal to −0.65 V, eq 6 yields an estimate for ΔG equal to −1.06 + 0.65 = −0.41 V or −410 mV. Finally, k_{et} is determined from ΔG using eq 11, yielding a value of 1.4×10^{-2} ps^{-1} (k_{et}^{-1} is thus 70 ps). Since E_{AR} is zero, eq 4 and 5 yield a value of α of 0.33 (Table III). Combining α and k_{et} results in a value of 212 ps for $(\alpha k_{et})^{-1}$.

$(Ru(TMB)_2(423\text{-}DQ^{2+}))^{4+}$. The onset of emission in the complex $Ru(TMB)_2(DMB)^{2+}$ (2.17 eV, Table IV) and the Ru 3+/2+ potential (+1.06 V, Table I) are substituted into eq 7, yielding a value of 1.06 − 2.17 = −1.11 V for the Ru 2+*/3+ potential. For this complex, the adjacent MLCT energy is lower than that of remote, so eq 6 is used to find ΔG. This yields a value of −1.11 + 0.65 = −0.46 V, or −460 mV, for ΔG. Equation 11 then yields an estimate of k_{et} equal to $2.31 \times 10\ 10^{-2}$ ps^{-1} (k_{et}^{-1} = 43 ps). Equations 4 and 5, with $E_{AR} = -100$ mV, yield a value of 0.96 for α (Table III). Combining this quantity with k_{et}^{-1}, $(\alpha k_{et})^{-1}$ is estimated to be 45 ps.

$(Ru(bpy)(423\text{-}DQ^{2+})_2)^{6+}$. The emission onset in $Ru(bpy)(DMB)_2^{2+}$ (2.16 eV, Table IV) and the Ru 3+/2+ potential (+1.19 V, Table I) are combined using eq 7 to give a value of 1.19 − 2.16 = −0.97 V for the Ru 2+*/3+ potential. Equation 8 is employed to estimate ΔG in this complex, since the adjacent MLCT energy is greater than remote. E_{AR} was found to be 0.05 V, and the DQ^{2+} (2+/1+) potential is −0.65 V. Equation 8 thus yields a value of ΔG equal to −0.97 + 0.65 − 0.05 = −0.37 V or −370 mV. Equation 11 then yields an estimate of k_{et} of 9.7×10^{-3} ps^{-1}, and k_{et}^{-1} is thus 103 ps. Equations 4 and 5, with E_{AR} = 50 mV, yield an α value of 0.21 (Table III). $(\alpha k_{et})^{-1}$ is thus estimated to be 490 ps.

$(Ru(bpy)(423\text{-}DQ^{2+})_2)^{6+}$. To estimate the Ru 2+*/3+ potential, the onset of emission in $Ru(DMB)_3^{2+}$ (2.19 eV, Table IV) and the Ru 3+/2+ reduction potential (+1.12 V, Table I) are combined using eq 7 to yield a value of 1.12 − 2.19 = −1.07 V. Equation 6 is employed for estimation of ΔG, with a DQ^{2+} (2+/1+) potential of −0.65 V. Thus ΔG is equal to −1.07 + 0.65 = −0.42 V, or −420 mV. Equation 11 yields a k_{et} estimate of 1.6×10^{-2} ps^{-1}, and k_{et}^{-1} is thus 63 ps. Equations 4 and 5, with E_{AR} = 50 mV, yield an α value of 0.67 (Table III), so $(\alpha k_{et})^{-1}$ is thus found to be 94 ps.

$(Ru(423\text{-}DQ^{2+})_3)^{8+}$. For this complex, there is a diquat electron acceptor on each ligand, so α is equal to unity. Using the emission onset in $Ru(DMB)_3^{2+}$ (2.19 eV) and the Ru 3+/2+ reduction potential of +1.15 V (Table I), the Ru 2+*/3+ potential is calculated to be −1.04 V. With the DQ^{2+} 2+/1+ reduction potential equal to −0.65, eq 6 yields a value of ΔG of −1.04 + 0.65 = −0.39 V, or −390 mV. k_{et}^{-1} is thus 85 ps. Since α is 1.0, k_f^{-1} is 85 ps, as well.

Appearance Potentials of $C_nH_{2n+2}N^+$ Ions (n = 1–3)

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Abstract: Considerable discrepancy exists in the literature over the appearance potentials for $C_nH_{2n+2}N^+$ ions arising from mono-, di-, and trimethylamine. Through observation of the reactions of the parent molecules with selected metal ions in a flow tube apparatus, both upper and lower limits are determined for the appearance potentials. For $AP(C_2H_6N^+)$ and $AP(C_3H_8N^+)$, 9.9 ± 0.1 eV is the upper limit and 9.2 ± 0.2 eV is the lower limit, while for CH_4N^+ the values are $9.9 \pm 0.1 \leqslant AP(CH_4N^+) \leqslant 10.6 \pm 0.1$ eV.

A number of values have been reported for the appearance potentials of certain $C_nH_{2n+2}N^+$ ions formed from amines. For example, in the case of the appearance of $C_2H_6N^+$ [$AP(C_2H_6N^+)$] from dimethylamine, the values range from 9.41 ± 0.06 to 10.50 eV.[1-3] Through new studies reported herein, we are able to provide both lower and upper limits for the appearance potentials of $C_2H_6N^+$ as well as CH_4N^+ and $C_3H_8N^+$ formed from mono-, di-, and trimethylamine (MMA, DMA, and TMA), respectively. The limiting values are derived from measurements of reactions of the parent molecules with selected metal ions.

Investigations[4] of the product distributions and mechanisms for the reaction of cobalt ion with a number of primary, secondary, and tertiary amines showed that, in each case, α-hydride abstraction to form neutral CoH and the $C_nH_{2n+2}N^+$ ion from the amine is a substantial, if not the major, reaction pathway. By analogy, recent studies in our laboratory of reactions of copper and silver ions are also consistent with an α-hydride abstraction mechanism for both DMA and TMA (also for MMA with copper ion), and we have been able to utilize these findings to determine the requisite appearance potentials as discussed in what follows.

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(1) Solka, B. H.; Russell, M. E. *J. Phys. Chem.* **1974**, *78*, 1268.

(2) Loudon A. G.; Webb, K. S. *Org. Mass Spectrom.* **1977**, *12*, 283.

(3) Taft, R. W.; Martin, R. H.; Lampe, F. W. *J. Am. Chem. Soc.* **1965**, *87*, 2490.

(4) Radecki, B. D.; Allison, J. *J. Am. Chem. Soc.* **1984**, *106*, 946.

0002-7863/88/1510-6682$01.50/0

Table I. Metal Ionization Potentials and Metal Hydride Dissociation Energies (eV)

	Pb	Ag	Cu
IP(M)	7.417[a]	7.576[b]	7.726[c]
$D_{298}°$(MH)	1.8 ± 0.2[d]	2.3 ± 0.1[d]	2.9 ± 0.1[e]
sum	9.2 ± 0.2	9.9 ± 0.1	10.6 ± 0.1

[a] Reference 10. [b] Reference 11. [c] Reference 12. [d] Reference 13. [e] Reference 14.

Experimental Section

In these investigations the reactions of amines with ground-state Cu^+, Ag^+, and Pb^+ are observed at room temperature, i.e., 298 K, in a flow reactor apparatus described previously.[5] Briefly, this apparatus consists of a flow tube (7.2-cm i.d., 104-cm length), an ion-sampling region, and a differentially pumped detection region. Metal ions are produced by thermionic emission and allowed to react with amine molecules introduced 74 cm upstream from the sampling orifice. The reaction mixture is sampled with a 1.0-mm-aperture platinum-sampling orifice, and the reactant and product ions are mass filtered with a quadrupole (Extrel). Ion detection occurs via pulse counting with a channeltron electron multiplier (Galileo Model 4830), preamplifier discriminator (Mech-Tronics PAD Model 509), and multichannel analyzer (Norland IT-5300). Differential pumping is maintained with a 650 L/s (Alcatel crystal 160) and a 300 L/s diffusion pump (Alcatel crystal 100).

The carrier gas (helium in these experiments) is introduced into the flow tube at a mass flow rate of about 10 000 sccm (MKS 259 flow controller, 20 000 sccm capacity). The flow tube pressure (monitored with a MKS 222B Baratron) is maintained at a selected value between 0.2 and 1.0 Torr by a fast roots pump (Stokes Pennwalt Model 1721).

The raw data consist of the flow tube pressure, temperature, and the m/z ratio of the initial product of each reaction. Since the reactions discussed in this paper are all very fast, each reactant gas was diluted with helium in order that primary and secondary products might be more readily differentiated. The rate coefficients for silver and copper ion reacting with MMA, DMA, and TMA are to be included in a forthcoming publication.[6] The method of ion production and the relatively high pressures (0.2–1.0 Torr) help to ensure that reaction products and rate coefficients are those stemming from thermalized ground-state metal ions. Proof of ground-state ions is discussed below.

It is desirable to discover which product channel(s) is active in each case in order that the appearance potential of each abstraction product may be bracketed. The flow tube pressure was varied to help ensure that the product channel activity was not pressure dependent.

Neutral reagents are standard lecture bottle gases used without further purification. As before, helium is passed through liquid nitrogen cooled molecular sieve traps to circumvent water interference problems.

Results and Discussion

Whenever hydrogen is abstracted from either MMA or DMA in the presence of excess amine, a secondary bimolecular reaction is observed. Ions of composition $C_nH_{2n+2}N^+$ are observed to react with an additional amine molecule to form protonated amine by proton transfer from the ion to the neutral molecule. Munson[7] as well as Jones and Harrison[8] observed that this type of reaction is quite fast, with rate coefficients approaching those corresponding to the collisional rate. The observation that $C_3H_8N^+$ from TMA does not react further with TMA to give protonated amine, while $C_2H_6N^+$ from DMA (CH_4N^+ from MMA) reacts with DMA (MMA) to give protonated amine, seems to indicate that the proton that is transferred arises from a hydrogen that is nitrogen bound on the ion rather than carbon bound.[7] In contrast to MMA and DMA, TMA has no nitrogen-bound hydrogen.

Table II. AP($C_nH_{2n+2}N^+$) for Ions Arising from MMA, DMA, and TMA (eV)

	AP(CH_4N^+)	AP($C_2H_6N^+$)	AP($C_3H_8N^+$)
Loudon and Webb[a]	10.70	10.50	10.55[d]
Solka and Russell[b]		9.41	
Taft, Martin, and Lampe[c]	10.3 ± 0.1	10.1 ± 0.1	9.8 ± 0.1
this work			
upper limit	10.6 ± 0.1	9.9 ± 0.1	9.9 ± 0.1
lower limit	9.9 ± 0.1	9.2 ± 0.2	9.2 ± 0.2

[a] Reference 2. [b] Reference 1. [c] Reference 3. [d] As inferred from text.[2]

Table III. Energetics of Copper and Silver Chloride Ion Formation from Ground-State Metal Ions and Methyl Chloride

	Ag	Cu
–IP(M)	–7.576[a]	–7.726[e]
$-D_{298}°$(ClM)	–3.54[b]	–3.97 ± 0.05[f]
$+I$(MCl)	+10.08 (v)[c]	+10.7 ± 0.3[g]
$+D_{298}°$($ClCH_3$)	+3.64[d]	+3.64[d]
$M^+ + CH_3Cl \rightarrow MCl^+ + CH_3$	+2.60	+2.64 ± 0.35

[a] Reference 11. [b] Reference 17. [c] Reference 18. [d] Reference 19. [f] Reference 12. [g] Reference 20. [h] Reference 20.

Hydride abstraction from an amine by a metal ion can be represented by

$$M^+ + C_nH_{2n+3}N \rightarrow C_nH_{2n+2}N^+ + MH$$

where M represents a metal atom. A three-step thermodynamic process may be used to determine the exothermicity of these bimolecular reactions. That is

$$\Delta H_{\text{react}} = \text{AP}(C_nH_{2n+2}N^+) - \text{IP}(M) - D_{298}°(\text{MH})$$

Thus the appearance potential of the $C_nH_{2n+2}N^+$ ion from its $C_nH_{2n+3}N$ precursor should be equivalent to the sum of the ionization potential of the metal atom and the dissociation energy of the neutral metal hydride whenever the reaction is exactly thermoneutral. A summary of the latter two terms is found in Table I for the metals of interest.

Lead ion forms a simple ion–molecule adduct with each of the three methylamines, while silver ion does this only with MMA.[9] The bimolecular reaction channel appears to be endothermic for these four reactions. Under the conditions of these experiments all the reaction pairs would form ion–molecule adducts if it were not for the bimolecular abstraction channel that dominates whenever it is thermodynamically allowed. It could be argued that the reactions that did not occur are not necessarily endothermic but that some kinetic barrier is preventing observation of reaction. No such barrier is expected for the four reactions in question; i.e. ion–molecule reactions do not characteristically display barriers in the reaction channel. Certainly the case of Ag^+ with MMA bears this out. The analogous reactions of Ag^+ with each of DMA and TMA and also Cu^+ with all three methylamines exhibit hydride abstraction occurring at the collisional rate.[6] Thus, the occurrence of the abstraction reaction is almost certainly thermodynamically rather than kinetically controlled. When Table I is referred to, it is concluded that the appearance potential for $C_2H_6N^+$ from DMA and $C_3H_8N^+$ from TMA must each be less than 9.9 ± 0.1 eV and greater than 9.2 ± 0.2 eV, since these ions appear as products when Cu^+ and Ag^+ are reactants but not when Pb^+ is the reactant ion. Because Cu^+ abstracts hydrogen from MMA, but Ag^+ does not, Table I also shows that $9.9 \pm 0.1 \leq \text{AP}(CH_4N^+) \leq 10.6 \pm 0.1$ eV. Table II lists literature values and results from this work for AP($C_nH_{2n+2}N^+$).

Our results agree quite well with the values that Lampe and co-workers[3] measured for all three of these ions. Their values for

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(5) Castleman, A. W., Jr.; Weil, K. G.; Sigsworth, S. W.; Leuchtner, R. E.; Keesee, R. G. *J. Chem. Phys.* **1987**, *86*, 3829.

(6) Sigsworth S. W.; Castleman, A. W., Jr., submitted for publication in *J. Am. Chem. Soc.*

(7) Munson, M. S. B. *J. Phys. Chem.* **1966**, *70*, 2034.

(8) Jones, E. G.; Harrison, A. G. *Can. J. Chem.* **1967**, *45*, 3119.

(9) Note: A very small trace of the abstraction product is found for lead ion reacting with each of DMA and TMA. It may be the case that the extreme high-energy tail of the Boltzmann distribution of lead ions is at or just above the threshold energy required for the abstraction reaction to occur.

(10) Brown, C. M.; Tilford, S. G.; Ginter, M. L. *J. Opt. Soc. Am.* **1977**, *67*, 1240.

(11) Brown, C. M.; Ginter, M. L. *J. Opt. Soc. Am.* **1977**, *67*, 1323.

(12) Tondello, G. *J. Opt. Soc. Am.* **1973**, *63*, 346.

(13) Gaydon, A. G. *Dissociation Energies and Spectra of Diatomic Molecules*, 3rd ed.; Chapman and Hall: London, 1968.

(14) Bulewicz, E. M.; Sugden, T. M. *Trans. Faraday Soc.* **1956**, *52*, 1475.

Table IV. Energetics of Formation of Methyl Ion from Methyl Chloride and Ground-State Silver and Copper Ions (eV)

	Ag	Cu
$-\mathrm{IP}(\mathrm{M})$	-7.576^a	-7.726^f
$-D_{298}°(\mathrm{ClM})$	-3.54^b	$+3.97 \pm 0.05^g$
$+\mathrm{IP}(\mathrm{CH_3})$	$+9.81 \pm 0.02^c$	$+9.81 \pm 0.02^c$
$+D_{298}°(\mathrm{ClCH_3})$	$+3.64^d$	$+3.64^d$
$\mathrm{M^+ + CH_3Cl \rightarrow CH_3{}^+ + MCl}$	$+2.33 \pm 0.02$	$+1.75 \pm 0.07$

[a] Reference 11. [b] Reference 17. [c] Reference 21. [d] Reference 19. [f] Reference 12. [g] Reference 20.

AP(CH_4N^+) and AP($C_3H_8N^+$) are located between the upper and lower limits specified herein, while for AP($C_2H_6N^+$) the extreme upper end of our range overlaps the lower end of their energy spread. Solka and Russell[1] reported a value for AP($C_2H_6N^+$) that is midrange to our results. The most recent literature results, reported by Loudon and Webb,[2] give a value for AP(CH_4N^+) that is just at the extreme upper limit of our reported range. However, as can be seen from Table II, they give results about 0.5 eV greater than our upper limit for both AP($C_2H_6N^+$) and AP($C_3H_8N^+$). Since we had ground-state Ag^+ ions, we can assert that these two values should not be above 10.0 eV.

For proof of ground-state metal ions, we refer back to previous work concerning reactions of methyl halides with Ag^+ and Cu^+.[5] Both of these ions were observed to react with CH_3Cl to give only the simple metal ion–methyl chloride adduct as the initial product (other products were due only to sequential clustering reactions). Tables III and IV give the energetics for the bimolecular fragmentation reactions that are most likely to occur. As can be seen, formation of each of $CuCl^+$, $AgCl^+$, and $CH_3{}^+$ is unfavorable for ground-state Cu^+ and Ag^+ ions. If, however, one considers the first excited state, i.e. the $^3D_3$ state, of Cu^+ and Ag^+ (at 10.44 and 12.43 eV,[15] respectively), all four of the reactions become exothermic. For the case of the reaction of Cu^+ ($^3D_3$) with CH_3Cl to form $CuCl^+$ and methyl radical, the exothermicity is 0.07 eV. In fact, Jones and Staley[16] observed $CuCl^+$ as the initial product for this reaction in an ion cyclotron resonance (ICR) cell in which the Cu^+ ions were produced by laser volatilization/ionization of the metal. Since the reaction for ground-state Cu^+ is endothermic, the implication is that excited states of Cu^+ were responsible for their observation of $CuCl^+$ product. In the present work, the $CuCl^+$ product is not observed, and therefore we conclude that excited-state metal ions are absent.

In conclusion, we obtain 9.2 ± 0.2 eV as the lower limit and 9.9 ± 0.1 eV as the upper limit for both AP($C_2H_6N^+$) and AP($C_3H_8N^+$), while for CH_4N^+ we obtain $9.9 \pm 0.1 \leqslant \mathrm{AP}(\mathrm{CH_4N^+}) \leqslant 10.6 \pm 0.1$ eV.

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(15) Dyke, J. M.; Fayad, N. K.; Morris, A.; Trickle, I. R. *J. Phys. B* **1979,** *12,* 2985.

(16) Jones, R. W.; Staley R. H. *J. Am. Chem. Soc.* **1980,** *102,* 3794.

(17) Guggi, D. J.; Neubert, A.; Zmbov, K. F. *Conf. Int. Thermodyn. Chim., [C.R.], 4th* **1975,** *3,* 124. (As reported in: *CRC Handbook* 60th ed.; CRC: Boca Raton, FL, 1979–1980; p F-220.

(18) Berkowitz, J.; Batson, C. H.; Goodman, G. L. *J. Chem. Phys.* **1980,** *72,* 5829.

(19) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, 1970.

(20) Guido, M.; Gigli, G.; Balducci, G. *J. Chem. Phys.* **1972,** *57,* 3731.

(21) Jonathan, N. *Faraday Discuss. Chem. Soc.* **1972,** *54,* 64.

Quantitative Studies of the Effect of Added Acid and Base on the Sputtering of Organic Amines and Acids from Dilute Glycerol Solution

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Abstract: The addition of strong acids and strong bases to glycerol solutions of organic bases and acids, respectively, has been found to have significant effects on the yield of secondary ions that can be obtained by sputtering. The effects observed are not uniform, however, in that the analyte signal may be either enhanced or degraded by addition of the reagent. Some monofunctional analytes showed enhancement of signal. Polybasic and polyacidic analytes invariably showed strong reductions in secondary ion signal after treatment with acid or base, respectively. The effects observed can be correlated with changes in analyte surface activity (glycerol solubility) that occur when the reagent alters the charge state of the analyte. Drop weight measurements of relative surface tensions have been used to corroborate the trends observed in the SIMS data.

Attempts to improve the secondary ion mass spectrometry (SIMS) sensitivity for organic amines and acids by the addition of mineral acids and bases, respectively, has a long history.[1-4] Such treatments are part of a more general strategy called "reverse-derivatization", which includes all of the various techniques that may be employed to produce a "precharged" form of the analyte.

The general concept of reverse-derivatization as first described by Busch et al.[5] involves the deliberate attachment of polar groups to analyte molecules which initially lack significant polarity. Groups such as quaternary ammonium salts and carboxylic acids have proven especially useful.[4]

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(1) Benninghoven, A.; Sichtermann, W. K. *Anal. Chem.* **1978,** *50,* 1181.

(2) Keogh, T.; DeStefano, A. J. *Anal. Chem.* **1981,** *53,* 25.

(3) Barber, M.; Bordoli, R. S.; Elliott, G. J.; Sedgwick, R. D.; Tyler, A. N. *Anal. Chem.* **1982,** *54,* 645A.

(4) Busch, K. L.; Cooks, R. G. *Science* **1982,** *218,* 247.

(5) Busch, K. L.; Unger, S. E.; Vincze, A.; Cooks, R. G.; Keough, T. *J. Am. Chem. Soc.* **1982,** *104,* 1507.

0002-7863/88/1510-6684$01.50/0