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The reactivity of metallated nitrenium ions studied by FT-ICR

Michael J. Yurkovich [a], Penggao Duan [a], Ryan C. Shea [a], Michael A. Watkins [a], Sarah M. Mandell [b,1], Eric M. Tippmann [b,1], Sen Jason Li [a], Matthew S. Platz [b,1], Hilkka I. Kenttämaa [a,*]

[a] *Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907, USA*
[b] *Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, OH 43210, USA*

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ABSTRACT

The reactivity of two metallated nitrenium ions toward various substrates was examined in the gas phase. The nitrenium ions were generated by a reaction of benzoyl azide with laser-ablated Mg^+ or Cu^+ in a Fourier transform ion cyclotron resonance mass spectrometer. The two nitrenium ions show drastically different reactivity. While the Mg-nitrenium ion reacts by radical mechanisms (*e.g.*, H atom abstraction), the Cu-nitrenium ion follows non-radical pathways (*e.g.*, metal ion transfer).

1. Introduction

Metallated nitrenium ions (metal ion nitrene adducts) have been proposed as reactive intermediates since 1967 [1,2]. The earliest example of this research involved the copper catalyzed reaction of sulfonylnitrene precursors (*i.e.*, iminoiodanes) with C–H bonds in the highly efficient synthesis of aziridines [1,2]. Although computational [3,4] and experimental [5,6] studies provide support for the existence of metallated nitrenium ions, compelling evidence for their existence in condensed phases still does not exist [7]. In 1988, Freiser and coworkers were the first to isolate and study the reactivity of several transition metal-nitrenium ions in the gas phase by using Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR) [8]. The metallated nitrenium ions $CrNH^+$, VNH^+, and $FeNH^+$ were generated via oxidative addition of the metal ion to an N–H bond of NH_3 followed by dehydrogenation [8]. These nitrenium ions were found to be unreactive or react by proton and/or NH transfer (sometimes accompanied by O abstraction) with simple hydrocarbons, amines, elemental oxygen, and water [8]. Other studies published on metallated nitrenium ions in the gas phase include the examination of reactions of $FeNH^+$ with D_2, and the determination of the M^+–NH binding energies for V, Sc and Ti, as well as several iron clusters [9]. The only exothermic reaction reported for $FeNH^+$ and D_2 is NH transfer to D_2 to form Fe^+ and NHD_2. This research extends the above work to larger metallated nitrenium ions.

2. Experimental details

Generation of metallated nitrenium ions and examination of their reactivity in the gas phase was performed by using a Finnigan model FTMS 2001 dual cell FT-ICR mass spectrometer described previously [10,11]. For convenience, one cell of the dual cell instrument is referred to as the source cell and the other as the analyzer cell. A high-power laser-induced acoustic desorption (LIAD) probe [12] inserted into the source side of the instrument was employed for the generation of the metal ions. The probe focused the laser beam of a Nd:YAG laser (532 nm, 5 ns pulse width) via a series of optics onto the back side of foils (~10 μm) of different metals secured to the end of the laser probe. In a typical experiment, 5–50 laser pulses were fired, each with an energy of approximately 2.5 mJ at the backside of the metal foil. The piercing of the foil resulted in an abundance of metal ions within the source side of the mass spectrometer. The ablated metal ions were cooled for ~1 s via collisions with Ar gas pulsed into the cell (peak pressure $\sim 1 \times 10^{-5}$ Torr in the cell), and then transferred into the adjacent analyzer cell by grounding the conductance limit for 77–160 μs. The metal ions were isolated via stored waveform inverse Fourier transformation [13,14] (SWIFT) excitation pulses. The neutral azide precursor (1), which was synthesized via a known procedure [15], was introduced into the analyzer side of the instrument by a Varian leak valve (nominal pressure $\sim 2–3 \times 10^{-7}$ Torr). The isolated metal

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[*] Corresponding author. Tel.: +1 765 494 0882; fax: +1 765 494 0359.
E-mail addresses: platz.1@osu.edu (M.S. Platz), hilkka@purdue.edu (H.I. Kenttämaa).
[1] Tel.: +1 614 292 8908; fax: +1 614 292 3639.

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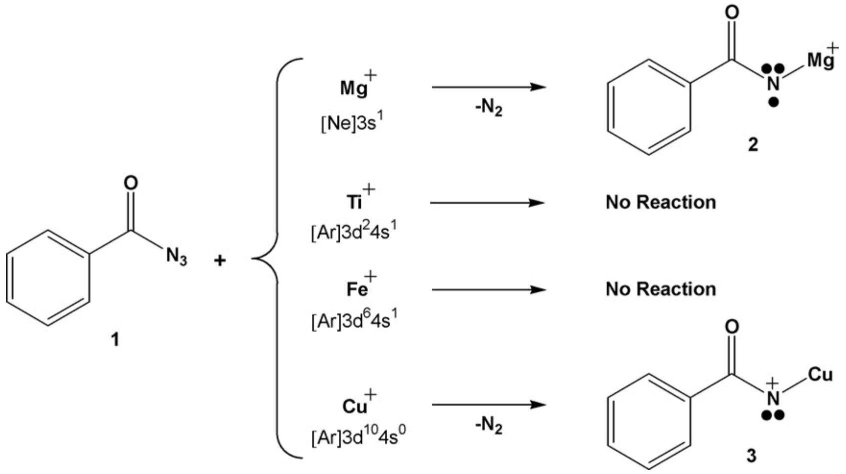


Scheme 1.

ions were allowed to react with **1** for 5–20 s, which for some metals yielded metallated nitrenium ions via loss of N_2 (Scheme 1). The metallated nitrenium ions were then transferred back into the source cell, cooled for about 1 s via collisions with argon gas pulsed into the cell (peak nominal pressure $\sim 1 \times 10^{-5}$ Torr in the cell), and isolated (vida supra), and allowed to react with selected neutral substrates for variable periods of time (0.005–30 s). Neutral substrates were introduced into the source cell by an Andonian variable leak valve. The nominal pressure of each neutral substrate was typically between 2.0×10^{-8} and 1.2×10^{-7} Torr, as measured by a Bayard-Alpert ionization gauge. Data acquisition and data analysis were carried out as described previously [16,17].

3. Results and discussion

3.1. Formation of metallated nitrenium ions

The metal ions Cu^+, Mg^+, Fe^+, and Ti^+ were chosen for this study. Of these, only Mg^+ and Cu^+ react with 1 to form metallated nitrenium ions (Scheme 1; note that the indicated charge is a formal charge dictated by the Lewis structure formalism and is not intended to indicate the location of the real charge, which almost certainly resides on the metal center). The ability of the Mg^+ and Cu^+ ions to form metallated nitrenium ions may be attributed to their small size or electron configuration. Formation of the odd-electron Mg-nitrenium ion (**2**) likely involves pairing of a nitrene electron with the $3s^1$ electron of Mg, giving it a full 3s orbital (and leaving a formally unpaired electron on the nitrogen atom). The donation of two electrons from the nitrene to the unoccupied 4s orbital of Cu produces an even-electron Cu-nitrenium ion (**3**), with completely full 3d and 4s orbitals on Cu (and no unpaired electrons). These configurations cannot be achieved by either Ti^+ or Fe^+.

3.2. Reactivity of metallated nitrenium ions

The reactivity of the Cu- and Mg-nitrenium ions toward several hydrocarbons, a halogenated hydrocarbon and two alcohols was examined (Tables 1 and 2). The observed reactions include H atom abstraction, adduct formation, and metal ion transfer. The Mg-nitrenium ion (2) reacts with cyclohexane and methylene chloride by H atom abstraction, with cyclohexene, tetramethylethylene, 1-hexyne and toluene by both H atom abstraction and adduct formation, and with methanol and ethanol by exclusive adduct formation. On the other hand, the Cu-nitrenium ion (**3**) is unreactive toward cyclohexane. It reacts with alcohols and methylene chloride exclusively to form a stable adduct, with 1-hexyne and toluene by exclusive metal ion transfer, and with alkenes by both pathways. Differences in the reactivities of the metallated nitrenium ions are discussed in detail below.

Perhaps the most significant reactivity difference for the two metallated nitrenium ions is the observation of H atom abstraction

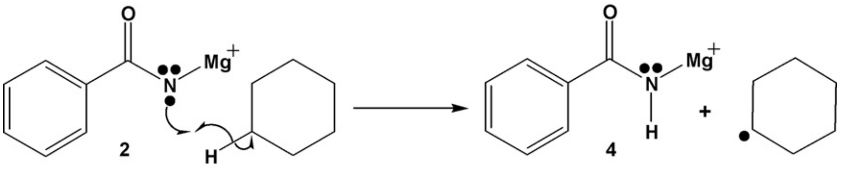
Table 1
The products formed in the reactions of the Mg-nitrenium ion (2) with an alkane, alkenes, an alkyne, an aromatic hydrocarbon, a halogenated hydrocarbon and alcohols.

Reagent (MW)	Observed product ions, *m*/*z* (%)	Reaction/product
Cyclohexane (84)	144 (100)	H atom abstraction
Tetramethylethylene (84)	144 (15)	H atom abstraction
	227 (85)	Adduct
Cyclohexene (82)	144 (22)	H atom abstraction
	225 (78)	Adduct
1-Hexyne (82)	144 (36)	H atom abstraction
	225 (64)	Adduct
Toluene (92)	144 (23)	H atom abstraction
	235 (77)	Adduct
Methylene chloride (84)	144 (100)	H atom abstraction
Methanol (32)	175 (100)	Adduct
Ethanol (46)	189 (100)	Adduct

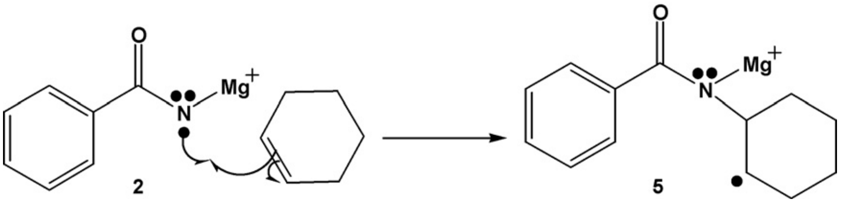
Table 2
The products formed in the reactions of the Cu-nitrenium ion (3) with an alkane, alkenes, an alkyne, an aromatic hydrocarbon, a halogenated hydrocarbon, and alcohols.

Reagent (MW)	Observed product ions, *m*/*z* (%)	Reaction/product
Cyclohexane (84)	No reaction	Not applicable
Tetramethylethylene (84)	147 (24)	Metal ion transfer (Cu^+ + alkene)
	266 (76)	Adduct
Cyclohexene (82)	145 (31)	Metal ion transfer (Cu^+ + alkene)
	(2°) 227[a]	Secondary addition (Cu^+ + 2 × alkene)
	264 (69)	Adduct
1-Hexyne (82)	145 (100)	Metal ion transfer (Cu^+ + alkene)
	(2°) 227[a]	Secondary addition (Cu^+ + 2 × alkene)
Toluene (92)	155 (100)	Metal ion transfer (Cu^+ + alkene)
Methylene chloride (84)	266 (100)	Adduct
Methanol (32)	214 (100)	Adduct
Ethanol (46)	228 (100)	Adduct

[a] Secondary products (2°) are listed after the primary product that formed them.



Scheme 2.



Scheme 3.

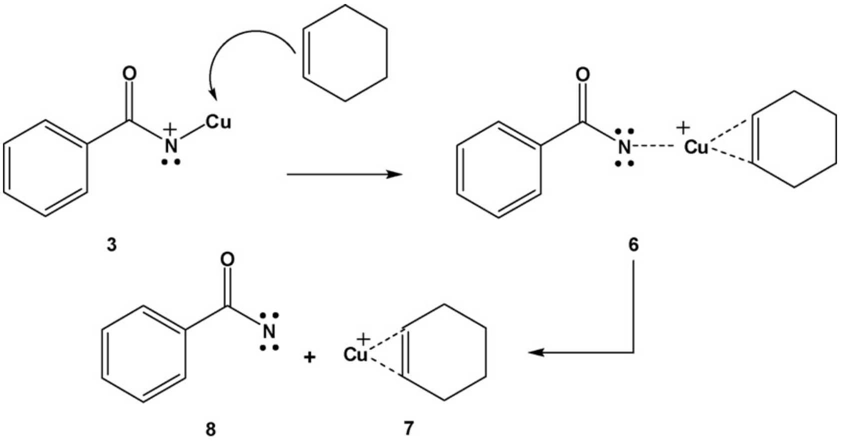
from the saturated hydrocarbon, cyclohexane, by the Mg-nitrenium ion (**2**) but a complete lack of reactivity toward cyclohexane for the Cu-nitrenium ion (**3**). This difference in reactivity supports the electron configurations assigned to the metallated nitrenium ions (Scheme 1). The odd-electron configuration of **2** permits it to react with cyclohexane by a radical mechanism (Scheme 2) while this is not possible for **3** due to its even-electron configuration. Indeed, **2** reacts with all hydrocarbons studied by H atom abstraction (Table 1). The experimentally determined lowest homolytic bond dissociation energies (BDE) for the C–H bonds in methylene chloride, methanol, cyclohexane, ethanol, toluene, cyclohexene, tetramethylethylene, and 1-hexyne are 99.0 ± 2 [18], 96.1 ± 0.2 [19], 95.5 ± 1 [18], 94.5 ± 2 [20], 89.8 ± 0.6 [19], 85 ± 1 [21], 78.0 ± 1.1 [18], and 73.2 ± 1.5 kcal/mol [18], respectively. Based on these values, and the observation of H atom abstraction for methylene chloride, it is thermochemically feasible for **2** to abstract a H atom from all the substrates studied. The ion-molecule collision complexes of the alcohols lie lower in energy than those of most of the other compounds due to their larger dipole moments (methanol and ethanol: 1.69 D and 1.70 D, respectively; methylene chloride: 1.60 D; all others: 0–0.87 D) [22]. Hence, these collision complexes have more energy available to overcome barriers. However, since no stable adduct was observed for methylene chloride, a compound with almost as large a dipole moment as the alcohols and substantially larger than those of the other compounds, this cannot be the reason for the observed behavior. Hence, the lack of H atom abstraction from the alcohols may be due to an especially strong interaction between the oxygen's lone pair and the metal ion in **2**.

Based on the above observations, the H atom affinity of **2** is very high, lying above 99 kcal/mol. This value is consistent with the nitrogen radical being the site that undergoes H atom abstraction in the metallated nitrenium ion (for example, the homolytic N–H BDE of benzamide is 103 kcal/mol [23]). It is concluded that H atom abstraction by the nitrogen atom in **2** produces **4** in an exothermic reaction.

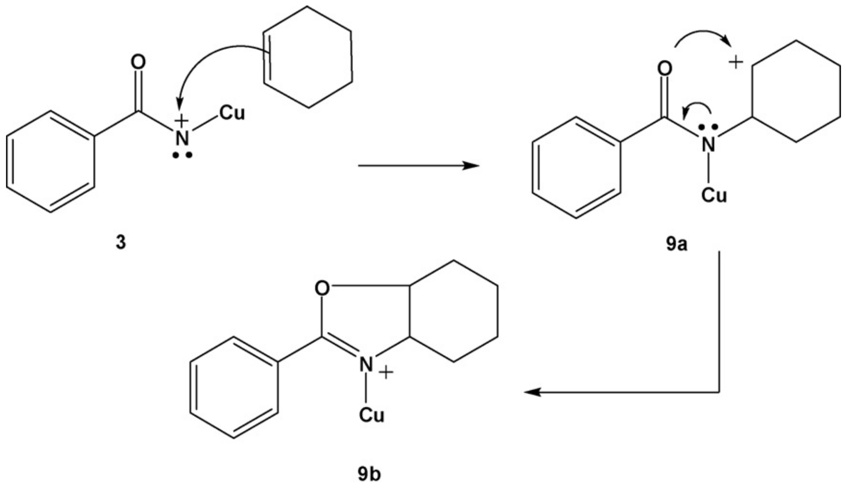
Based on the electron configuration of **2**, formation of stable adducts upon interaction of **2** with the unsaturated hydrocarbons could involve a radical addition mechanism (for cyclohexene, see Scheme 3). However, this mechanism is not possible for the alcohols due to lack of unsaturation. A different pathway, involving H atom abstraction by **2** from the alcohol, followed by addition of the new ketyl radical to the N-centered radical, seems unlikely since cyclohexane does not form a stable adduct. Hence, the adduct of **2** and alcohols is probably formed by coordination of the metal with a lone pair on oxygen.

H atom abstraction is a characteristic reaction of the odd-electron Mg-nitrenium ion (**2**), but metal ion transfer is common for the even-electron Cu-nitrenium ion (**3**). Clearly, the nature of the metal ion has a drastic influence on which part of the nitrene complex reacts (*i.e.*, Mg^+ activates the nitrogen atom while Cu^+ does not). Metal ion transfer occurs in reactions of **3** with all the unsaturated hydrocarbons but not for the saturated hydrocarbon, halogenated hydrocarbon or the alcohols. Scheme 4 presents a possible mechanism for metal ion transfer between **3** and cyclohexene.

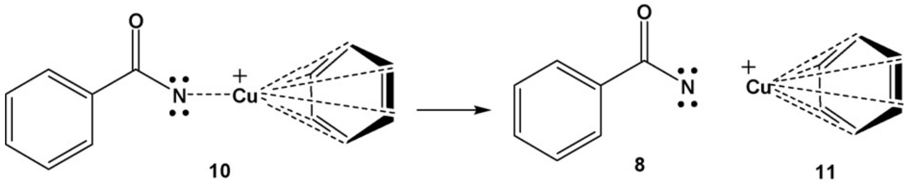
Although there are drastic differences in the reactivity of **2** and **3**, formation of a stable adduct was observed for both metallated



Scheme 4.



Scheme 5.



Scheme 6.

nitrenium ions with almost all substrates. Adduct formation can occur via a variety of mechanisms for **2**, as discussed above. To form a stable adduct with **3**, the nucleophile may add coordinatively to the metal center or to the unsaturated nitrogen atom, as shown in Schemes 4 and 5, respectively. The observation of metal ion transfer reactions for all unsaturated hydrocarbons demonstrates that these substrates can add to the metal ion. Whether attack also occurs on the nitrogen atom is not as obvious. For all the other substrates, the addition site is currently unknown.

Tables 1 and 2 show that while **2** forms an adduct with all nucleophiles except methylene chloride, **3** reacts this way only with tetramethylethylene, cyclohexene, methylene chloride, methanol, and ethanol. The lack of adduct formation for 1-hexyne and toluene as compared to the other hydrocarbons may be rationalized by their ability to form stronger bonds with free metal ions than the other nucleophiles. Scheme 6 provides a possible mechanism for the metal ion transfer reaction from **10** to toluene. Although all unsaturated hydrocarbons can electrostatically interact with a metal ion, the strength of the ion/π interaction [24,25] is dictated by the substituents, size, curvature, and composition of the π-system [26]. Due to the similarity of the unsaturated substrates studied here (similarly sized unsaturated hydrocarbons with no appreciative curvature (except for toluene) in their π-systems), steric hindrance and electron density should be the main reactivity controlling parameters in this study. Based on electron density, the ion/π interactions for 1-hexyne and toluene (π-4 and π-6, respectively) are predicted to be stronger [26] than those for tetramethylethylene and cyclohexene (π-2 for both). In fact, it was recently shown that the Cu^+/toluene π-6 interaction is extremely strong [26]. The greater strength of these bonds may explain why the adducts formed between toluene or 1-hexyne and 3 fragment to metal ion transfer products instead of relaxation via emission of IR radiation [27].

The absence of metal ion transfer products in the reactions of **3** with alcohols, cyclohexane and methylene chloride may arise from the stability of complexes such as **6** with these reagents due to their poorer ability to interact with free metal ions. A recent study has shown that the binding energies of Cu^+ with various organic substrates correlate with the substrates' experimental proton affinities (PA) [28]. The PAs for tetramethylethylene, 1-hexyne, cyclohexene, ethanol, methanol, cyclohexane, and methylene chloride are 194.5 [29], 191.2 [29], 187.5 [29], 185.6 [29], 180.3 [29], 164.2 [29], and 148.6 kcal/mol [30], respectively (tolene is not considered here since it forms a π-adduct with metal ions [26]). Indeed, the alcohols, cyclohexane, and the halogenated hydrocarbon have the lowest PAs. The binding energies of Cu^+ for toluene, ethene and methanol have been measured to be 52.3, 42.7 and 42.6 kcal/mol, respectively [31]. This trend does not correlate with the PAs (187.4 [29], 162.6 [29] and 180.3 [29], respectively). However, it supports the proposal that toluene interacts more strongly with a free Cu^+ ion than alcohols and alkenes.

As discussed above, metal ion transfer reactions occur between the metallated nitrene ion **3** and all of the unsaturated hydrocarbons. However, only the metal ion adducts of cyclohexene and 1-hexyne undergo a secondary reaction by the addition of another substrate molecule ($Cu^+ + 2 \times$ alkene). This reactivity is rationalized by the strong ion/π-interaction and lack of steric hindrance for 1-hexyne and cyclohexene.

4. Conclusions

Based on above results, it can be concluded that the metal ion has a strong influence on the reactivity of metallated nitrenium ions. The reactions of the Mg- and Cu-nitrenium ions with the studied substrates involve radical and non-radical pathways, respectively, yielding characteristic reaction products for each nitrenium ion. Hence, the electron configuration of the metallated nitrenium ion appears to dictate its reactivity.

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References

[1] H. Kwart, A.A. Khan, J. Am. Chem. Soc. 89 (1967) 1950–1951.
[2] H. Kwart, A.A. Khan, J. Am. Chem. Soc. 89 (1967) 1951–1953.
[3] P. Brandt, M.J. Soedergren, P.G. Andersson, P.-O. Norrby, J. Am. Chem. Soc. 122 (2000) 8013–8020.
[4] K.M. Gillespie, E.J. Crust, R.J. Deeth, P. Scott, Chem. Commun. (Cambridge, UK) (2001) 785–786.
[5] Z. Li, R.W. Quan, E.N. Jacobsen, J. Am. Chem. Soc. 117 (1995) 5889–5890.
[6] M.M. Diaz-Requejo, P.J. Perez, M. Brookhart, J.L. Templeton, Organometallics 16 (1997) 4399–4402.
[7] X. Lin, C.-M. Che, D.L. Phillips, J. Org. Chem. 73 (2008) 529–537.
[8] S.W. Buckner, J.R. Gord, B.S. Freiser, J. Am. Chem. Soc. 110 (1988) 6606–6612.
[9] (a) D.E. Clemmer, L.S. Sunderlin, P.B. Armentrout, J. Phys. Chem. 94 (1990) 208–217;
(b) D.E. Clemmer, L.S. Sunderlin, P.B. Armentrout, J. Phys. Chem. 94 (1990) 3008–3015;
(c) R. Liyanage, J.B. Griffin, P.B. Armentrout, J. Chem. Phys. 119 (2003) 8979–8995;
(d) R. Liyanage, P.B. Armentrout, Int. J. Mass Spectrom. 241 (2005) 243–260.
[10] K.K. Thoen, H.I. Kenttämaa, J. Am. Chem. Soc. 121 (1999) 800–805.
[11] J.M. Price, K.E. Nizzi, J.L. Campbell, H.I. Kenttämaa, M. Seierstad, C.J. Cramer, J. Am. Chem. Soc. 125 (2003) 131–140.
[12] R.C. Shea, S.C. Habicht, W.E. Vaughn, H.I. Kenttämaa, Anal. Chem. 79 (2007) 2688–2694.
[13] A.G. Marshall, T.C.L. Wang, T.L. Ricca, J. Am. Chem. Soc. 107 (1985) 7893–7897.
[14] A.G. Marshall, T.L. Ricca, T.-C.L. Wang, Patent Application: US, Ohio State University Research Foundation, USA, 1988, p. 23.
[15] D.S. Bose, A.V.N. Reddy, Tetrahedron Lett. 44 (2003) 3543–3545.
[16] J.L. Campbell, K.E. Crawford, H.I. Kenttämaa, Anal. Chem. 76 (2004) 959–963.
[17] J.L. Campbell, M.N.M.N. Fiddler, K.E. Crawford, P.P. Gqamana, H.I. Kenttämaa, Anal. Chem. 77 (2005) 4020–4026.
[18] D.F. McMillen, D.M. Golden, Annu. Rev. Phys. Chem. 33 (1982) 493–532.
[19] S.J. Blanksby, G.B. Ellison, Acc. Chem. Res. 36 (2003) 255–263.
[20] B. Ruscic, J. Berkowitz, J. Chem. Phys. 101 (1994) 10936–10946.
[21] Z.B. Alfassi, L. Feldman, Int. J. Chem. Kinet. 13 (1981) 771–783.
[22] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 71st ed., CRC Press, Boston, 1990.
[23] N.R. Wijeratne, P.G. Wenthold, J. Phys. Chem. A 111 (2007) 10712–10716.
[24] D.A. Dougherty, Science 271 (1996) 163–168.
[25] J.P. Gallivan, D.A. Dougherty, Proc. Natl. Acad. Sci. U.S.A. 96 (1999) 9459–9464.
[26] C. Ruan, Z. Yang, M.T. Rodgers, Phys. Chem. Chem. Phys. 9 (2007) 5902–5918.
[27] R.C. Dunbar, J. Phys. Chem. A 106 (2002) 9809–9819.
[28] Z. Safi, A.M. Lamsabhi, J. Phys. Chem. A 111 (2007) 2213–2219.
[29] S.G. Lias, Ionization energy evaluation, in: P.J. Linstrom, W.G. Mallard (Eds.), NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg, MD, 2005, http://webbook.nist.gov.
[30] Calculated at G3 level of theory.
[31] (a) M.R. Sievers, L.M. Jarvis, P.B. Armentrout, J. Am. Chem. Soc. 120 (1998) 1891–1899;
(b) Z. Yang, N.S. Rannulu, Y. Chu, M.T. Rodgers, J. Phys. Chem. A 112 (2008) 388–401.