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Dissociation behavior of Cu(urea)$^+$ complexes generated by electrospray ionization

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Dedicated to Dr. Yannik Hoppilliard on the occasion of her 60th birthday.

Abstract

Electrospray ionization of aqueous solutions of Cu(II) salts in the presence of urea is used to generate the monoligated copper(I) cation Cu(urea)$^+$. To this end, the cone voltage is appropriately adjusted, thereby affording extensive collision-induced fragmentations of the multiply ligated ions evolving from solution. Among the wide range of transition-metal complexes studied during the two last decades, the dissociation behavior of Cu(urea)$^+$ is exceptional, because the product distributions significantly deviate from expectation based on thermochemical criteria only. While fully confirming previous experimental and theoretical studies of Luna et al. [J. Phys. Chem. A 104 (2000) 3132], the present results add a note of caution to the uncritical application of kinetic methods to the competitive dissociation of transition-metal complexes. (Int J Mass Spectrom 219 (2002) 729–738)

Keywords: Copper; Electrospray ionization; Kinetic method; Mass spectrometry; Urea

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1. Introduction

Two years ago, Luna et al. [1] reported a combined experimental and theoretical study on the unimolecular and collision-induced dissociations (CID) of the Cu(urea)$^+$ cation, **1**, in the gas-phase. While most results were in pleasing agreement with previous findings [2–12] on the gas-phase chemistry of monoligated copper(I) species Cu(L)$^+$, one aspect appeared particularly intriguing to us, not only with respect to the specific behavior of Cu(L)$^+$ species, but also for the gas-phase ion chemistry of transition-metal complexes in general.

In particular, Luna et al. reported that energized **1** reacts via C–N bond cleavage concomitant with hydrogen migration to produce Cu(NH$_3$)$^+$ and Cu(HNCO)$^+$, respectively, as ionic fragments. Both fragmentations are complementary to each other in that ammonia leaves while HNCO retains at the copper center in (1a), whereas the opposite applies for (1b). It is therefore quite reasonable to assume that in the course of the reaction a common, bisligated intermediate is formed, i.e., (H$_3$N)Cu(HNCO)$^+$.

$$\mathrm{Cu(urea)^+ \rightarrow Cu(HNCO)^+ + NH_3} \qquad (1a)$$

$$\mathrm{Cu(urea)^+ \rightarrow Cu(NH_3)^+ + HNCO} \qquad (1b)$$

Experimentally, Luna et al. found reaction (1a) to clearly predominate over reaction (1b) in both

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metastable ion and CID spectra of $Cu(urea)^+$. However, according to their accompanying theoretical studies ammonia is bound more strongly to copper than HNCO by about 17 kcal/mol [1,3]. While one might question these theoretical predictions, the level of theory used, i.e., B3LYP/6-311+G(2df,2p), is considered reliable because it yields good to excellent results for similar $Cu(L)^+$ ions [2–6]. Moreover, the computed trend of the copper-ion affinities of NH_3 and HNCO is supported by reference to the proton affinities, $PA(NH_3) = 204$ kcal/mol and $PA(HNCO) = 180$ kcal/mol [13], keeping in mind that copper-ion affinities and *PA*s are known to correlate quite well [14]. Accordingly, the decay of energized $Cu(urea)^+$ appears to be an example for a case in which the relative intensities of two formally directly competing reactions, i.e., (1a) and (1b), do not follow thermochemical criteria, but are instead seriously affected by reaction dynamics. While such a conclusion is not too uncommon for small inorganic and organic ions, it is quite surprising to encounter such a situation in transition-metal ion chemistry for it implies that the complex $(H_3N)Cu(HNCO)^+$ is unlikely to serve as an intermediate en route to dissociation of **1**. In a more general context, this finding suggests that the commonly assumed formation of long-lived complexes in the gas-phase chemistry of transition-metal ions deserves a critical evaluation [15–17].

However, before generally questioning a well-established concept in gas-phase ion chemistry on the basis of a single experimental observation, a reinvestigation of the $Cu(urea)^+$ system by a complementary technique is indicated. More precisely, while there are no obvious indications, one cannot strictly rule out that the CI-FAB method used by Luna et al. [1] might lead to the formation of electronically excited species for which ground-state considerations do not apply. Here, electrospray ionization (ESI) of diluted aqueous solutions of copper(II) salts and urea is used as an alternative method for the generation of **1**.

A second facet concerns the loss of water from gaseous **1** according to reaction (2), a process addressed only briefly by Luna et al. [1]. As outlined below, also the characteristics of this particular dissociation channel pose some fundamental questions with respect to the interpretation of the fragmentation behavior of mass-selected transition-metal ion complexes.

$$Cu(urea)^+ \rightarrow [Cu, C, H_2, N_2]^+ + H_2O \qquad (2)$$

2. Experimental methods

The experiments used a VG BIO-Q mass spectrometer which was gratefully supplied as a gift from the Aventis Pharma (Frankfurt/Main). Because it is a commercial instrument, a short description of the essential features may suffice. The VG BIO-Q consists of an ESI source combined with a tandem mass spectrometer of QHQ configuration (Q = quadrupole, H = hexapole). In the present experiments, millimolar solutions of urea and Cu(II) salts (i.e., $CuCl_2$ and $Cu(NO_3)_2$) in either pure water or methanol/water (1:1 mixture with 0.5% formic acid) were introduced through a stainless steel capillary to the ESI source via a syringe pump (ca. 5 μL/min). Nitrogen was used as nebulizing and drying gas at source temperatures between 60 and 150 °C.

The ions formed upon electrospray were sampled at adjustable cone voltages (U_C), thereby allowing to control the extent of fragmentation in the source region [18–20]. The larger the cone voltage, the more excessive fragmentations occur, and atomic Cu^+ prevails for $U_C \geq 50$ V (see below). Overview mass spectra of the ions formed were obtained at unit mass resolution by scanning Q1. For CID, the ions of interest, here $Cu(urea)^+$, were mass-selected using Q1, interacted with nitrogen as a collision gas in the hexapole at variable collision energies ($E_{lab} = 0$–50 eV), while scanning Q2 to monitor the ionic products. As the VG BIO-Q is primarily destined for biochemical applications, it is not equipped with differential pumping in the analyzer region. As a consequence, the collision gas may not only be present in the hexapole collision cell, but also in other parts of the analyzer where the ions move with higher energies. Nevertheless, the instrument is designed adequately enough such that negligible fragmentation of $Cu(urea)^+$ occurs at $E_{\mathrm{lab}} = 0$ eV. For a semi-quantitative analysis of the energy-dependent CID experiments, the collision energies were converted to the center-of-mass frame, $E_{\mathrm{CM}} = m/(M+m)E_{\mathrm{lab}}$, where m and M stand for the masses of the collision gas and the ionic species, respectively. In order to ensure that the experiments were not obscured by multiple collision events, CID spectra were recorded at different pressures (0.3–1 mTorr) for which no notable differences were found within the errors margins given below. For the time being, some limitations in hardware and software do not permit threshold CID experiments in a manner similar to the procedures introduced by Armentrout and coworkers [21]. Specifically, neither a quantitative determination of the cross sections nor a dedicated scan of E_{lab} in a multiple-ion monitoring mode are feasible. Further, the width of the kinetic energy distribution in the hexapole (ca. 0.4 eV at half peak height) has not been unconvoluted from the data. Therefore, the data remain semi-quantitative so far. In the present experiments, separate CID spectra at fixed collision energies were recorded at unit mass resolution, and the intensities given below refer to the integrated peak areas of the fragment ions indicated. The appearance energies given below are averages of three independent measurements, where the uncertainties include the spread of the separate data, the neglect of thermal contributions, and the limited number of data points, not to mention more subtle phenomena such as lifetime effects [21]. Another, practically more relevant modification suggested by the present study is the replacement of the stainless steel of the ESI capillary by other material because steel shows limited resistance against corrosion by the Cu(II) solutions.

3. Results and discussion

Under more or less standard conditions, ESI of aqueous millimolar solutions of copper(II) salts CuX_2 (X = Cl and NO_3) and urea gives rise to the solvated ions $[CuX(H_2O)_m(urea)_n]^+$ with $m + n = 2, 3$; selected examples are given in Fig. 1a and b for X = NO_3 which are recorded at cone voltages of $U_C = 10$ and 20 V, respectively. While increased solvation ($m + n > 3$) can be achieved by further modification of the source conditions, this was deliberately not pursued because monoligated species are of interest here. The intensity of the urea complexes is of comparable magnitude as those of the pure water complexes ($n = 0$), although water, as the solvent, is present in a huge excess. This result indicates preferential binding of the metal ion to urea, as already implied by the computational studies of Luna et al. [1,3]. The desired formation of monoligated $Cu(L)^+$ ions requires desolvation and reduction to Cu(I) which both are achieved by increasing U_C above the standard range of 0–20 V. With rising U_C, the monoligated copper(II) ions $CuX(H_2O)^+$ and $CuX(urea)^+$ prevail, which then loose X rather than the closed-shell ligands to inter alia form $Cu(urea)^+$, for which acceptable yields were obtained between $U_C = 40$ and 70 V (Fig. 1c). Further increase of U_C also causes dissociation of the monoligated ions to yield bare Cu^+ (Fig. 1d). Details of the interesting competition between desolvation (evaporation of closed-shell ligands) and redox steps (losses of X radicals) will be addressed in a forthcoming study. While the trends emerging from Fig. 1 can be regarded as representative, the relative ion abundancies very much depend on the experimental parameters, such as gas flows, concentrations and flow rates of the solution, source temperatures, and the nature of X. For example, reasonable amounts of $Cu(urea)_2{}^+$ can be produced at higher concentrations of urea, whereas this particular ion does not exceed the lower percent level under the conditions typical for the spectra shown in Fig. 1.

In the following, let us concentrate on the CID spectra of mass-selected $Cu(urea)^+$ in the QHQ instrument. To this end, the cone voltage is adjusted to 40–70 V, i.e., the range in which sufficient intensities of **1** are achieved. Fig. 2 summarizes the CID spectra of $Cu(urea)^+$ at various collision energies given in the center-of-mass frame (E_{CM}). At $E_{\mathrm{CM}} = 0$ eV, no dissociation is detectable. Fragmentation commences at $E_{\mathrm{CM}} \approx 1$ eV, where $Cu(HNCO)^+$ and $Cu(NH_3)^+$ corresponding to reaction (1a) and (1b) are observed along with

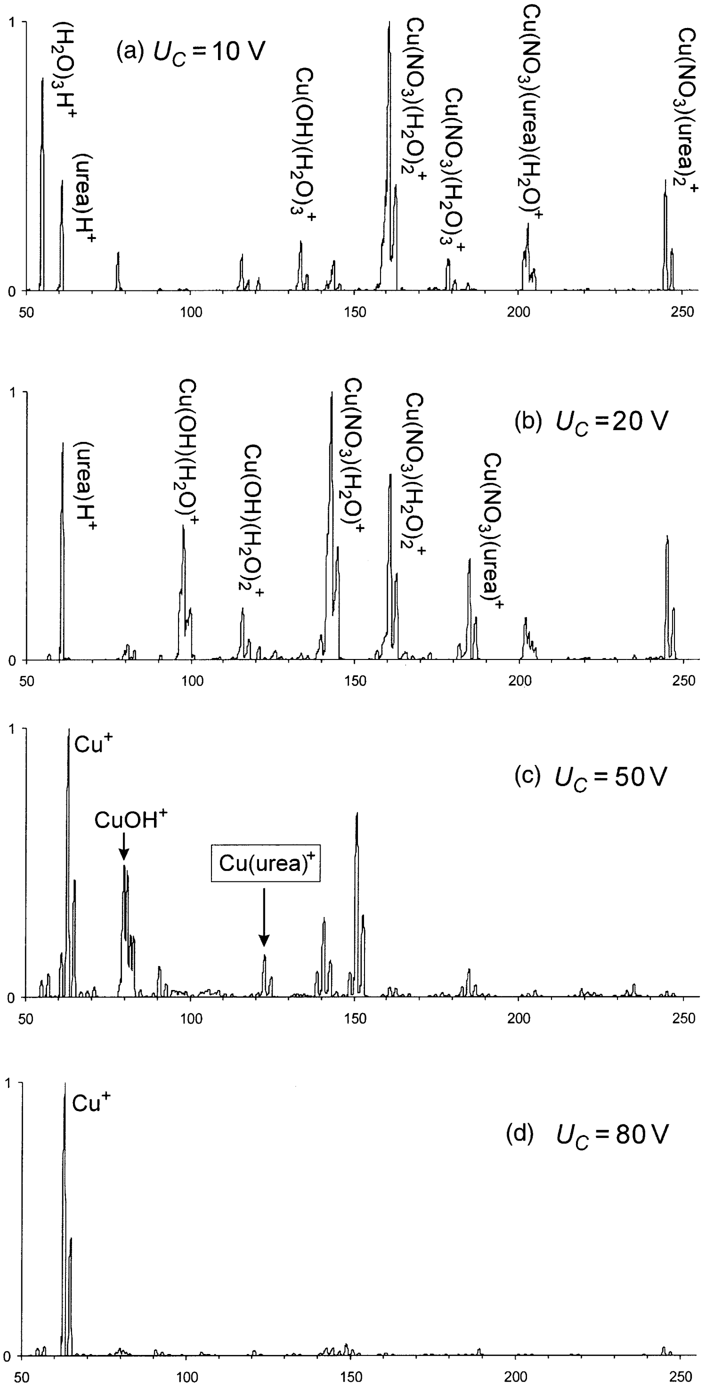


Fig. 1. ESI spectra (from 50 to 255 amu) of an aqueous solution of $Cu(NO_3)_2$ and urea (both ca. 2 mmol/L) at variable cone voltages: (a) $U_C = 10$ V, (b) $U_C = 20$ V, (c) $U_C = 50$ V, and (d) $U_C = 80$ V.

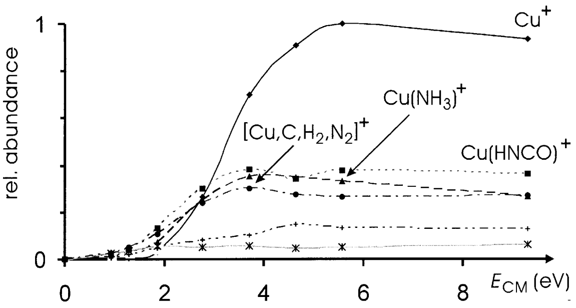


Fig. 2. Fragment ions formed upon CID of mass-selected $Cu(urea)^+$ at variable collision energies (collision gas: N_2 at 0.47 mTorr): Cu^+ (◆), $Cu(NH_3)^+$ (▲), $Cu(HNCO)^+$ (■), $[Cu, C, H_2, N_2]^+$ (●), $Cu(H_2O)^+$ (+), and $Cu(N_2)^+$ and/or isobaric $Cu(CO)^+$ (both: ✱).

loss of water (reaction (2)). These three processes increase in intensity with increasing collision energies up to $E_{CM} \approx 3\,eV$ at which formation of Cu^+ begins to predominate (reaction (3)). The latter process corresponds to simple loss of the ligand from **1** and can therefore effectively compete with the rearrangements involved in reactions (1) and (2), if the collision energies significantly exceed the bond-dissociation energy $D_0(Cu^+–urea)$. This competition of rearrangements, reflected by the losses of NH_3, H_2O, and HNCO, respectively, and direct detachment of the intact urea ligand is fully consistent with [1], except for the notably more abundant loss of water in our experiments (see below).

$$Cu(urea)^+ \rightarrow Cu^+ + urea \tag{3}$$

While not being analyzed any further, Fig. 2 also displays two minor channels which are assigned to $Cu(H_2O)^+$, the complementary ionic product of reaction (2), $Cu(CO)^+$ which was also observed in the CID spectrum in [1], and/or $Cu(N_2)^+$ which can be attributed to collisionally driven exchange of the urea ligand by nitrogen used as a collision gas.

Because a rigorous quantitative threshold analysis of the CID data cannot be performed for the time being (see experimental section), crude estimates for the appearance energies (*AE*s) of the ionic fragments evolving from **1** were derived by extrapolation of the linear parts of the signal onsets in Fig. 2, leading to: $AE[Cu, C, H_2, N_2]^+ = 1.2 \pm 0.5$, $AE(Cu(HNCO)^+) = 1.3 \pm 0.5$, $AE(Cu(NH_3)^+) = 1.4 \pm 0.5$, and $AE(Cu^+) = 2.1 \pm 0.5\,eV$. Compared to threshold energies, the certainly most serious systematic perturbation is associated with the internal energy of the precursor ions. While ESI itself is often assumed to yield more or less thermal ions, the particular conditions chosen to generate the monoligated complex $Cu(urea)^+$ deliberately involve energizing collisions in the cone region. Consequently, the appearance energies are likely to be underestimated relative to the reaction thresholds at 0 K (E_0). Relative to $Cu(urea)^+$, the computational studies of Luna et al. [1] predict $E_0(Cu(NH_3)^+) = 0.78$, $E_0(Cu(HNCO)^+) = 1.54$, and $E_0(Cu^+) = 2.70\,eV$, respectively, while noting that the occurrence of reaction (1) requires passage of a barrier located 2.27 eV above ground-state $Cu(urea)^+$; loss of water was not included in the computational survey. Because the agreement between experimental data and theoretical predictions for $D_0(Cu^+–L)$ is quite good [1–12,21], we may use the computed $D_0(Cu^+–urea) = 2.70\,eV$ [1] as a reference for further discussion. Not unexpectedly, the appearance energy $AE(Cu^+) = 2.1 \pm 0.5\,eV$ determined in our experiments is somewhat lower than the computational prediction. Assuming a similar difference of about 0.6 eV for the other dissociation channels as well, we arrive at thresholds of about 2 eV for reactions (1a), (1b), and (2). More important than quantitative considerations is the qualitative finding that losses of NH_3 and HNCO (reactions (1a) and (1b)) compete with each other once significant fragmentation is observed. In fact, the $Cu(HNCO)^+$ fragment even tends to prevail at low collision energies (Fig. 3). This observation fully confirms the results of Luna et al. [1] and reinforces their implicit conclusion that the transition structures (TSs) associated with the dissociation of energized $Cu(urea)^+$ cause the deviation from expectation based on thermochemical criteria only: even though NH_3 is more strongly bound to Cu^+ than HNCO, reactions (1a) and (1b) compete with each other already at the very onset of fragmentation. The experimental results described here therefore confirm the theoretical prediction of Luna et al. that the

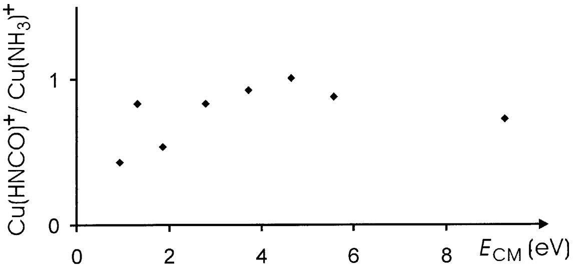


Fig. 3. Ratio of $Cu(HNCO)^+$ and $Cu(NH_3)^+$ fragments generated upon CID of mass-selected $Cu(urea)^+$ at variable collision energies (collision gas: N_2 at 0.47 mTorr).

putative complex $(H_3N)Cu(HNCO)^+$ is not involved as an intermediate in the dissociation of energized **1**. Consequently, the dissociation of $Cu(urea)^+$ does indeed represent an example for a failure to describe the dissociation of an ionic transition-metal complex in terms of thermochemical arguments. By means of theory, Luna et al. [1] have provided an internally consistent mechanistic rationale for the particular behavior of $Cu(urea)^+$.

Finally, loss of water (reaction (2)) is addressed in some more detail, because it reveals yet another puzzling aspect of the $Cu(urea)^+$ system. Actually, we were suspicious about reaction (2) right from the beginning because the experimental data of Luna et al. contained some counterintuitive information. Thus, the CI-FAB mass spectra communicated in [1] show notable signals due to loss of H_2O occurring in the ion source ($m/z = 105$ and 107 with the correct $^{63}Cu/^{65}Cu$ isotope pattern), whereas loss of ammonia ($m/z = 106$ and 108) hardly is discernible. In contrast, the MI and CID spectra of mass-selected $Cu(urea)^+$ recorded by Luna et al. exhibit predominant eliminations of NH_3 rather than H_2O. A priori, it is difficult to trace these conflicting observations back to a certain physicochemical origin, because several phenomena might be involved. Nevertheless, it may indicate either (i) that H_2O loss is particularly sensitive to the internal energy content of $Cu(urea)^+$ or (ii) that the species fragmenting in the source somehow structurally differ from the mass-selected ions. As the energy behavior in Fig. 2 gives no indications for the former, the latter option is probed by CID experiments in the ESI instrument in which the collision conditions are kept constant while those of ionization are varied, e.g., different cone voltages, counterions, and solvents. While some minor differences emerge from these experiments, a clear trend towards preferential elimination of H_2O at higher cone voltages is found under all conditions (Table 1); the ratio of NH_3 and H_2O losses (last column) is particularly instructive in this respect.

The mere observation of such a dependence of the CID spectra on the source conditions unequivocally proves that different populations of isobaric and/or isomeric ions are sampled in these experiments. While the limited mass resolution of quadrupole analyzers does not allow to resolve isobaric ions, this possibility is unlikely in the present case. Rather, preferential water loss at higher cone voltages is observed for the $Cu(urea)^+$ ions of both copper isotopes with variable counterions and solvents. Hence, the occurrence of reaction (2) is attributed to a collision-induced isomerization of $Cu(urea)^+$ in the cone region. Before continuing with the implications of this line of reasoning, the structure of the $[Cu, C, H_2, N_2]^+$ species formed in reaction (2) is addressed. Assuming that the N–C–N connectivity of urea remains intact upon elimination of water, $[Cu, C, H_2, N_2]^+$ may either correspond to a cyanamide complex $Cu(H_2NCN)^+$ formed via hydrogen migration followed by a 1,2′-elimination or a carbodiimide complex $Cu(HNCNH)^+$ originating from an alternative path of hydrogen migration and subsequent 1,2′-elimination (Scheme 1). For these product ions, an earlier computational study of Luna et al. [2] predict heats of formation of $\Delta H_f(Cu(H_2NCN)^+) = 225 \pm 2$ and $\Delta H_f(Cu(HNCNH)^+) = 237 \pm 2$ kcal/mol. Using $\Delta H_f(H_2O) = -57.8$ kcal/mol [22] and the reasonable assumption [2,7,21,23] that $D_0(H_2NCNCu^+–H_2O) \approx D_0(HNCNHCu^+–H_2O) \approx D_0(Cu^+–H_2O) = 1.69$ eV [3], the heats of formation of the putatively involved isomers can be estimated as $\Delta H_f((H_2O)Cu(H_2NCN)^+) = 128$ and $\Delta H_f((H_2O)Cu(HNCNH)^+) = 140$ kcal/mol, respectively. Hence, these bisligated ions have similar stabilities as $Cu(urea)^+$, for which $\Delta H_f(Cu(urea)^+) = 138$ kcal/mol is obtained from $\Delta H_f(Cu^+) = 259$, $\Delta H_f(urea) = -58.8$ kcal/mol

Table 1
Relative fragment ion abundancies upon CID (E_{lab} = 15 eV, collision gas: N_2) of mass-selected $Cu(urea)^+$ generated from different solutions at variable cone voltages (U_C in V)

Ion mass[a]	U_C	$Cu(HNCO)^+$	$Cu(H_2NCN)^+$[b]	$Cu(H_2O)^+$	$Cu(NH_3)^+$	$-NH_3/-H_2O$[c]
$Cu(NO_3)_2$/urea in H_2O						
123	47	105	65	10	65	1.6
123	58	50	85	15	55	0.6
125	58	55	105	15	65	0.5
123	69	55	320	30	65	0.2
$CuCl_2$/urea in H_2O						
123	53	85	45	7	140	1.9
123	67	95	110	12	75	0.9
125	67	90	125	10	65	0.7
$CuCl_2$/urea in 1:1 CH_3OH/H_2O with 0.5% HCOOH						
123	43	100	50	5	105	2.0
123	55	70	60	8	70	1.2
123	66	90	110	12	70	0.8

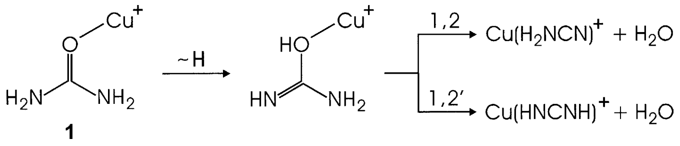
Relative fragment ion abundancies normalized to the Cu^+ signal deliberately set to 100. The copper(II) salts and urea were both present in millimolar concentrations in the different solutions.

[a] The ions with m/z = 123 and 125 amu correspond to the ^{63}Cu and ^{65}Cu isotopes of $Cu(urea)^+$.

[b] See text for the discussion of the structural assignment.

[c] Ratio of $Cu(HNCO)^+$ and $Cu(H_2NCN)^+$ signals.

[22], and $D_0(Cu^+–urea) = 2.70$ eV [1]. Accordingly, the isomerizations $Cu(urea)^+ \rightarrow (H_2O)Cu(H_2NCN)^+$ and $Cu(urea)^+ \rightarrow (H_2O)Cu(HNCNH)^+$ appear conceivable. Nevertheless, a collision-induced isomerization alone cannot account for the experimental findings because it would only occur efficiently, if the associated barrier were low. In such a case, however, reaction (2) should neither show an energy-dependence similar to those of the other fragmentations shown in Fig. 2 nor depend on the cone voltage. These observations lead to the suggestion that the isomerization $Cu(urea)^+ \rightarrow (H_2O)Cu(H_2NCN)^+$ and/or $(H_2O)Cu(HNCNH)^+$ is quasi-irreversible upon collision with N_2, whereas in the cone region it is mediated by proton catalysis involving the excess of protic solvents (water, methanol). In a more general sense, these results suggest that the CID patterns of ions generated by ESI must not necessarily evolve from the isomer(s) anticipated to be present in solution. Similarly, source conditions might have favored isomerization in the CI-FAB experiments of Luna et al. [1], thereby explaining the notably different intensities of NH_3 and H_2O losses in the ion source compared to the dissociations of mass-selected **1**. Interestingly, among the few previous reports on the “unexpected” formation of isomeric transition-metal complexes in gas-phase experiments [19,24,25], also another example deals with an HNCO complex of copper, i.e., generation of $(C_3H_6)Cu(HNCO)^+$ rather than $Cu(C_3H_7NCO)^+$ in ion/molecule reactions of bare Cu^+ with propylisocyanate [26].



Scheme 1.

4. Perspectives

The present results fully confirm the observation of Luna et al. [1] that the branching ratio of reactions (1a) and (1b) upon dissociation of energized Cu(urea)$^+$ does not correlate with reaction thermochemistry. Obviously, the branching ratio is controlled by kinetic phenomena as elucidated in detail by the theoretical studies in [1]. Nevertheless, the specific behavior of **1** may simply be regarded as an exception. From a conceptual point of view, however, these results pose nontrivial problems to organometallic reaction mechanisms in general and the application of kinetic methods [27] to the dissociation of transition-metal complexes in particular. Let us briefly discuss some hypothetical potential-energy surfaces to illustrate these aspects.

Consider a species A–M$^+$–B where M is a metal, A and B are ligands capable to react to a new species C, thereby forming the isomeric ion M$^+$–C. In the present case, this reads as A = NH$_3$, B = HNCO or A = H$_2$NCN, B = H$_2$O with M = Cu and C = urea. Provided that the energy demand of the TS associated with the isomerization A–M$^+$–B $\rightleftarrows$ M$^+$–C is lower than the thresholds for losses of A, B, and C, respectively (Fig. 4a), interconversion is rapid compared to dissociation such that CID of the mass-selected ions yields "correct" thermochemical thresholds and branching ratios. The problem begins when the isomerization barrier approaches D(A–MB$^+$) and D(AM$^+$–B) because excited M$^+$–C might then behave as "hot" A–M–B$^+$ and hence show a different branching ratio. In the hypothetical case of Fig. 4b, for example, at the very threshold A–M$^+$–B only yields A–M$^+$ + B, whereas dissociation of energized M$^+$–C might also lead to A + M$^+$–B. In the extreme (Fig. 4c), the barrier is above both dissociation channels such that dissociation of energized M$^+$–C may approach a 1:1 ratio of A–M$^+$ + B and A + M$^+$–B. While these scenarios are already nontrivial, the

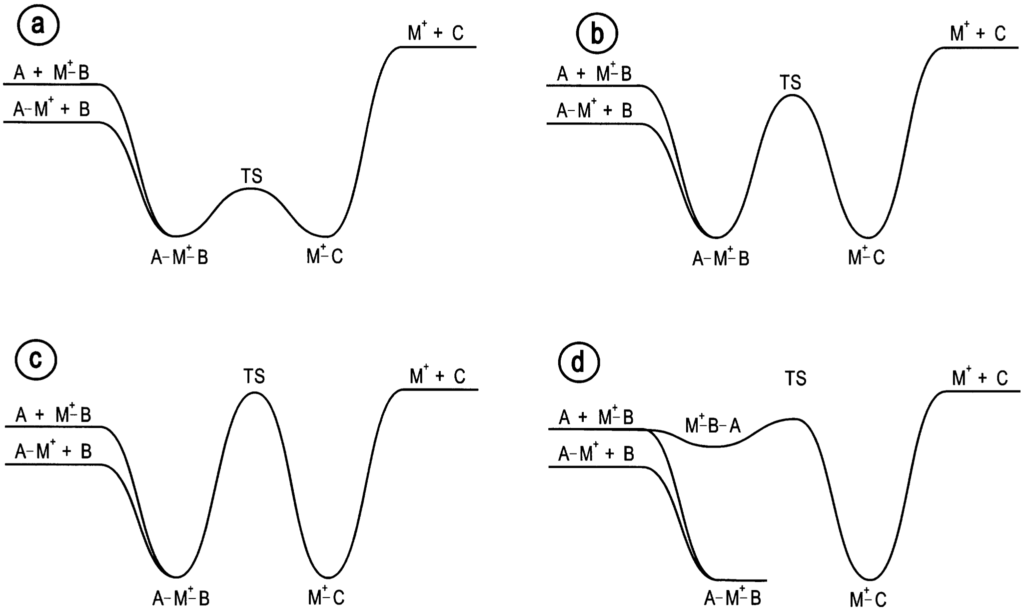


Fig. 4. Hypothetical potential-energy surfaces of a bisligated metal ion A–M$^+$–B and its isomer M$^+$–C connected by a TS with an activation energy E_a: (a) $E_a \ll D(\mathrm{AM^+–B}) < D(\mathrm{A–MB^+}) < D(\mathrm{M^+–C})$, (b) $D(\mathrm{AM^+}–B) < E_a \approx D(\mathrm{A–MB^+}) < D(\mathrm{M^+–C})$, and (c) $D(\mathrm{AM^+–B}) < D(\mathrm{A–MB^+}) \ll E_a \approx D\ (\mathrm{M^+–C})$. (d) Schematically simplified situation for Cu(urea)$^+$ dissociation (with M = Cu, A = NH$_3$, B = HNCO, and C = urea) according to the calculations of Luna et al. [1].

potential-energy surface of Cu(urea)$^+$ computed by Luna et al. [1] even includes a further aspect in that the lowest-lying TS is directly linked with only one of the two possible dissociation asymptotes. Fig. 4d gives a simplified sketch of this situation; see [1] for details. In practice, the Cu$^+$/urea system turns out to be even more complex due to the involvement of yet another species, most likely $(H_2O)Cu(H_2NCN)^+$, formed in an apparently quasi-irreversible process in the ion source (see above).

From a purist point of view, these results seriously question the application of kinetic methods to competitive dissociations of ionic transition-metal complexes and seem to require an explicit and reliable theoretical treatment in each case. Nevertheless, there exist some practical guidelines to evaluate the occurrence of situations such as depicted in Fig. 4b and d. At first, the ligands A and B must be able to combine to a reasonably stable species C. Hence, the above scenario is only likely, if at least one ligand bears a multiple bond (or a strained ring system). Next, control experiments aimed to independently generate the isomers A–M$^+$–B and M$^+$–C can be used to rule out isomerization, provided that M$^+$–C bears an additional fragmentation channel which is not observed for A–M$^+$–B. Even if the dissociation channels do not differ, degenerate ligand-exchange using isotopically labeled ligands can be used to chemically probe the ion structure(s); note, however, that this approach is nontrivial, because the probe itself might induce isomerization [28]. Finally, the whole line of arguments raised above about the dissociation of Cu(urea)$^+$ is associated with the fact that the isomerization barriers are rather large. In this respect, the Cu$^+$ cation having a quasi closed-shell s^0d^{10} configuration differs from other (open-shell) transition-metal ions. In fact, while reaction mechanisms are generally similar, gaseous Cu$^+$ involves larger barrier compared to most other 3d metal ions [26,29–31]. In summary, the application of kinetic methods is certainly justified for competitive dissociation of most transition-metal complexes, but at least a qualitative consideration of the above scenarios is recommended to evaluate the appropriateness of the experimental approaches.

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References

[1] A. Luna, B. Amekraz, J.-P. Morizur, J. Tortajada, O. Mó, M. Yáñez, J. Phys. Chem. A 104 (2000) 3132.
[2] A. Luna, B. Amekraz, J.-P. Morizur, J. Tortajada, O. Mó, M. Yáñez, J. Phys. Chem. A 101 (1997) 5931.
[3] A. Luna, B. Amekraz, J. Tortajada, Chem. Phys. Lett. 266 (1997) 31.
[4] A. Luna, B. Amekraz, J. Tortajada, J.-P. Morizur, M. Alcamí, O. Mó, M. Yáñez, J. Am. Chem. Soc. 120 (1998) 5411.
[5] A. Luna, J.-P. Morizur, J. Tortajada, M. Alcamí, O. Mó, M. Yáñez, J. Phys. Chem. A 102 (1998) 4652.
[6] M. Alcamí, O. Mó, M. Yáñez, A. Luna, J.-P. Morizur, J. Tortajada, J. Phys. Chem. A 102 (1998) 10120.
[7] A. Luna, M. Alcamí, O. Mó, M. Yáñez, Int. J. Mass Spectrom. 201 (2000) 215.
[8] C.W. Bauschlicher Jr., S.R. Langhoff, in: A. Fontijn (Ed.), Gas-Phase Metal Reactions, North-Holland, Amsterdam, 1992, p. 277.
[9] H. Lavanant, Y. Hoppilliard, J. Mass Spectrom. 32 (1997) 1037.
[10] S. Hoyau, G. Ohanessian, Chem. Phys. Lett. 280 (1997) 266.
[11] N. Fröhlich, G. Frenking, in: J. Cioslowski (Ed.), Quantum-Mechanical Prediction of Thermochemical Data, Kluwer, Dordrecht, 2001, p. 199.
[12] T. Shoeib, C.F. Rodriguez, K.W.M. Siu, A.C. Hopkinson, Phys. Chem. Chem. Phys. 3 (2001) 853.
[13] E.P.L. Hunter, S.G. Lias, J. Chem. Phys. Ref. Data 27 (1998) 413.
[14] R.W. Jones, R.H. Staley, J. Am. Chem. Soc. 1904 (1982) 2296.
[15] J. Allison, D.P. Ridge, J. Am. Chem. Soc. 101 (1979) 4998.
[16] R.W. Jones, R.H. Staley, J. Am. Chem. Soc. 102 (1980) 3794.
[17] D.A. Weil, C.L. Wilkins, J. Am. Chem. Soc. 107 (1985) 7316.
[18] M. Kohler, J.A. Leary, Int. J. Mass Spectrom. Ion Processes 162 (1997) 17.
[19] F. Rogalewicz, Y. Hoppilliard, G. Ohanessian, Int. J. Mass Spectrom. 201 (2000) 307.
[20] P.J. Dyson, A.K. Hearly, B.F.G. Johnson, T. Khimyak, J.S. McIndoe, P.R.R. Langridge-Smith, C. Whyte, Rapid Commun. Mass Spectrom. 15 (2001) 895, and references therein.

[21] H. Koizumi, X.G. Zhang, P.B. Armentrout, J. Phys. Chem. A. 105 (2001) 2444, and references cited therein.

[22] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (Suppl. 1) (1998).

[23] K. Koszinowski, D. Schröder, H. Schwarz, M.C. Holthausen, J. Sauer, H. Koizumi, P.B. Armentrout, submitted for publication.

[24] Y. Hoppilliard, F. Rogalewicz, G. Ohanessian, Int. J. Mass Spectrom. 204 (2001) 267.

[25] F. Rogalewicz, Y. Hoppilliard, G. Ohanessian, Int. J. Mass Spectrom. 206 (2001) 45.

[26] K. Eller, H. Schwarz, Int. J. Mass Spectrom. Ion Processes 108 (1991) 87.

[27] R.G. Cooks, P.S.H. Wong, Acc. Chem. Res. 31 (1998) 379.

[28] H. Becker, D. Schröder, W. Zummack, H. Schwarz, J. Am. Chem. Soc. 116 (1994) 1096.

[29] R. Tonkyn, M. Ronan, J.C. Weisshaar, J. Phys. Chem. 92 (1988) 92.

[30] A. Dahrouch, H. Mestdagh, C. Rolando, J. Chem. Phys. 91 (1994) 443.

[31] K. Seemeyer, D. Schröder, M. Kempf, O. Lettau, J. Müller, H. Schwarz, Organometallics 14 (1995) 4465.