A robust link between the thermochemistry of urea and isocyanic acid by dissociative photoionization

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**Abstract**

Dissociative photoionization reactions of internal energy selected urea cations were studied by vacuum ultraviolet threshold photoionization at the imaging photoelectron photoion coincidence (iPEPICO) endstation of the VUV beamline at the Swiss Light Source. An accurate $T = 0 \, \text{K}$ appearance energy could be determined for the lowest energy channel, the formation of isocyanic acid (HNCO) and ammonia cation (NH$_3^+$). This process is analogous to the thermolysis of urea in selective catalytic reduction (SCR) for which $\Delta H^f_{298} = (62.9 \pm 1.0) \, \text{kJ} \cdot \text{mol}^{-1}$ is derived. The next higher energy channel leading to H$_2$NCO$^+$ and NH$_3$ is also discussed. The parent ion was found to dissociate quickly to HNCO + NH$_3$ even at threshold, indicating a loose transition state. The potential energy surface of a roaming H atom around the urea core shows lower H-transfer barriers in the cation than in the neutral molecule, and the measured dissociative photoionization energy is lower than expected based on the literature enthalpies of formation. Consequently, the threshold for HNCO loss corresponds to the dissociative photoionization energy and not to a prior H-transfer barrier. A significant, 5.1 kJ·mol$^{-1}$ discrepancy between the dissociation energy and the reaction energy calculated with the latest published values of the enthalpy of formation warrants a revision of the urea and isocyanic acid thermochemistry. This discrepancy is assigned to enthalpies of formation with the help of W1 and CBS-APNO ab initio calculations. The isocyanic acid enthalpy of formation at $T = 0 \, \text{K}$ and that of gas phase urea at $T = 298 \, \text{K}$ are, thus, revised to $\Delta H^f_{298}(\text{HNCO}, \text{g}) = -(116.2 \pm 1.4) \, \text{kJ} \cdot \text{mol}^{-1}$ and $\Delta H^f_{298}(\text{CO(NH}_2)_2, \text{g}) = -(235.7 \pm 1.4) \, \text{kJ} \cdot \text{mol}^{-1}$, respectively.

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1. Introduction

Urea was first synthesized in 1828 by Wöhler [1], a discovery that contributed to the end of vitalism and the birth of organic chemistry. In 2010, the yearly urea production was 1.5·10$^{11}$ kg, i.e., more than 20 kg per person, most of which is used in agriculture as fertilizer [2]. Among its numerous other applications, it is now routinely used in selective catalytic reduction (SCR) processes to reduce nitrogen oxide emissions of diesel vehicles [3–5]. The reducing agent in this process is ammonia, which is released in two steps: (1) by the thermolysis of urea and (2) by catalytic hydrolysis of the resulting isocyanic acid (HNCO). The role of gas phase urea in SCR has been addressed by Bernhard et al. [6].

Davies et al. reviewed urea thermochemistry in 1991 [7], and reported a standard urea enthalpy of formation of $-(333.59 \pm 0.21) \, \text{kJ} \cdot \text{mol}^{-1}$ [8] in conjunction with a sublimation enthalpy of $(87.9 \pm 2.1) \, \text{kJ} \cdot \text{mol}^{-1}$ [9], yielding $\Delta H^f_{298}(\text{g}) = -(245.6 \pm 2.1) \, \text{kJ} \cdot \text{mol}^{-1}$. In a study of urea derivatives, da Silva et al. used $\Delta H^f_{298}(\text{g}) = -(245.8 \pm 1.2) \, \text{kJ} \cdot \text{mol}^{-1}$ [10]. More recent phase change measurements [6,11], however, scatter around a significantly higher sublimation enthalpy value with the most recent $T = 298 \, \text{K}$ value being $(95.5 \pm 0.3) \, \text{kJ} \cdot \text{mol}^{-1}$ [12]. Consequently, $\Delta H^f_{298}(\text{g}) = -(238.1 \pm 0.4) \, \text{kJ} \cdot \text{mol}^{-1}$ appears to be the current $T = 298 \, \text{K}$ gas phase urea heat of formation, which lies just outside the uncertainty range of $-(235.5 \pm 1.2) \, \text{kJ} \cdot \text{mol}^{-1}$, listed in the NIST Chemistry Webbook [13]. The first three electronic states overlap in the photoelectron spectrum of urea [14], complicating the assignment of the adiabatic ionization energy. In a photoionization mass spectrometry study [15], Wenzheng et al. determined a 9.85 eV onset to urea photoionization.

Isocyanic acid (HNCO) was also discovered by Liebig and Wöhler [16]. In addition to being an intermediate in SCR processes, the chemistry of [HNCO] isomers in interstellar clouds has recently gained interest [17]. The isocyanic acid $\Delta H^f$ in the NIST Chemistry Webbook [13] is based on the NIST-JANAF compilation value [18], $\Delta H^f_{298}(\text{HNCO}, \text{g}) = -(98.7 \pm 8) \, \text{kJ} \cdot \text{mol}^{-1}$, which is derived from the onset for the photodissociation reaction HNCO → NH(c$^2 \Sigma^+$) + CO (X $^3\Sigma^+$) [19,20] and a thermochemical cycle involving $\Delta H^f(\text{NCO}^-, \text{aq})$. In congruence with later spectroscopic studies (vide infra), we will conclude that this value, although still persisting in the thermochemical literature [21] and being used to benchmark ab initio
thermochrometry methods [22], is too high. Zhang et al. reported
\( \Delta H^0_{\text{f}}(\text{HNCO}, g) = -(117.1 \pm 4.2) \text{ kJ} \cdot \text{mol}^{-1} \) based on an N–H dissociation threshold measurement [23].

At present, the experimental thermochrometry of isocyanic acid appears best established via the dissociation threshold for HNCO → NH(a 1Δg) + CO \((X (\Sigma^+))\), using \( T = 0 \text{ K} \) enthalpies of formation for NH (imidogen) and CO of \( (358.7 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1} \) and \( -(113.81 \pm 0.03) \text{ kJ} \cdot \text{mol}^{-1} \), respectively [24]. The imidogen ground state is triplet, and the singlet–triplet separation of 151.8 \text{ kJ} \cdot \text{mol}^{-1} [25,26] has to be taken into account to establish the product energy of \( (396.7 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1} \). Spiglanin et al. determined a dissociation energy of 41 530 cm\(^{-1}\) \((496.8 \pm 2.4) \text{ kJ} \cdot \text{mol}^{-1} \) [27], based on experimental data that Zyrnianov et al. claimed also are reconcilable with an onset of \( (42 700 \pm 200) \text{ cm}^{-1} \) \((510.8 \pm 2.4) \text{ kJ} \cdot \text{mol}^{-1} \) [28].

In the same paper, they reported a threshold of \( (42 840 \pm 100) \text{ cm}^{-1} \) \((512.5 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1} \) [28], which they later revised to 
\( (42 750 \pm 25) \text{ cm}^{-1} \) \((511.4 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1} \) based on photofragment ion imaging experiments [29]. This latter value is in good agreement with the Brown et al. upper limit \( D_0(\text{HN–CO}) \leq (42 710 \pm 100) \text{ cm}^{-1} \) \((510.9 \pm 1.2) \text{ kJ} \cdot \text{mol}^{-1} \) [30]. The best experimental \( T = 0 \text{ K} \) isotopic acid enthalpy of formation is, thus, \( \Delta H^0_{\text{f}}(\text{HNCO}, g) = (396.7 – 511.4) \text{ kJ} \cdot \text{mol}^{-1} \). This can be compared with the \( \text{ab initio} \) result of East et al. of \( -(114.6 \pm 2) \text{ kJ} \cdot \text{mol}^{-1} \) dating from 1993 [31], updated to \( -(115.5) \text{ kJ} \cdot \text{mol}^{-1} \) in a more recent focal point analysis of NCO and [HNCO] isomers [32].

We will show that low internal energy urea cations undergo dissociative photoionization to produce \( \text{NH}_2^+ \) and HNCO, mirroring the thermolysis step in SCR [33], whereas high internal energy cations lose \( \text{NH}_3 \) by \( \text{C–N} \) bond rupture. Both the enthalpy of formation and the adiabatic ionization energy of ammonia are very well known \( \Delta H^0_{\text{f}}(\text{NH}_3, g) = -(38.57 \pm 0.03) \text{ kJ} \cdot \text{mol}^{-1} \) [24] and \( I_{\text{ad}}(\text{NH}_3) = 10.186385 \text{ eV} \pm 191 \mu\text{eV} \) (982.83 kJ \cdot \text{mol}^{-1} ) [34]. Thus, accurate onset energies for the dissociative photoionization processes of urea can shed light on the underlying thermochrometry of urea and isocyanic acid inSCR. Invoking the ion cycle to address this issue has two distinct benefits. First, it tackles the uncertainty about the enthalpy of sublimation of urea, as well as independently confirming the neutral spectroscopy results for isocyanic acid. Second, calorimetric urea experiments are referenced to room temperature, whereas spectroscopic methods yield \( T = 0 \text{ K} \) energy levels. Thus, \( T = 0 \text{ K} \) and \( T = 298 \text{ K} \) are connected by our method.

In single photon threshold photoionization, i.e., when no kinetic energy is imparted on the photoelectron or the photon, all excess energy above the adiabatic ionization energy is deposited as internal energy of the parent ion: \( E_{\text{ion}} = h\nu – I_{\text{ad}} + E_{\text{neutral}} \). The radiative lifetime is usually much longer than the experimental timescale [35]. Thus, the internal energy can be redistributed statistically, and the density of states is dominated by the ground electronic ion state [36]. Therefore, the ground state potential energy surface is sampled for energetically and entropically allowed decay processes as a function of ion internal energy. These processes can in turn be modelled by statistical theory [37,38] to derive accurate dissociative photoionization onsets, which are then used in thermochemical cycles to obtain, e.g., enthalpies of formation [39,40], proton affinities [41,42], isomerization energies [43] or bond energies [44,45] with sub kJ \cdot \text{mol}^{-1} accuracy in favourable cases.

The production of \( \text{NH}_2^+ \) represents the lowest energy dissociative photoionization channel in urea. It is a fast channel, and \( \text{H} \) migration takes place readily in low internal energy parent ions. Since isomerization precedes dissociation, we must ask if the measured threshold energy truly corresponds to the dissociative photoionization energy or to the isomerization barrier. This prompted us to look at the potential energy surface more in detail, similarly to previous work on \( \text{H} \) migration in trimethyl pnictogens [46].

2. Experimental

Only an overview is given of the Imaging Photoelectron Photoion Coincidence (iPEPICO) experiment, and the reader is referred to a previous description for more details [47]. Urea has mass fraction purity 0.99 Riedel-de Haen was brought into the gas phase by an oven source, heated to 110 °C providing a sufficient sample vapour pressure of 2 \cdot 10^{-4} \text{ Pa}. Isolated urea molecules were ionized by the incident synchrotron radiation within a 2 - 2 mm spot at the VUV beam line [48] of the Swiss Light Source before its upgrade [49]. The photon energy was calibrated against 115–148 Å argon auto ionization lines, both in the first and second order. The photoelectrons are velocity map imaged onto a DLD40 Roentdek position sensitive delay-line detector with a kinetic energy resolution better than 1 meV at threshold. The photoions are extracted by the 80 V \cdot \text{cm}^{-1} \text{ field in a 5 cm long first acceleration region, after which they are further accelerated to } -1160 \text{ V to space focus them at a Jordan TOF C-726 microchannel plate detector.} The time-of-flight (TOF) mass analysis of the photo ions is carried out by using the electron hits as start signals, and correlating the electron events with the ion hits in an arbitrary TOF window in a multiple-start/multiple-stop coincidence acquisition setup [50].

Because the electrons are imaged according to their off-axis momentum, some energetic (hot) electrons are detected in the central spot, thereby contaminating the true threshold (zero kinetic energy) electron signal. The hot electron contamination is accounted for by subtracting mass spectra associated with electrons collected in a small ring around the central spot with typical inner and outer diameters of 0.8 and 1–1.5 mm, respectively, from the centre, threshold signal [51]. Based on the autoionization line widths, the photon energy resolution is expected to be 3–4 meV, but the centre and ring areas were chosen so as to correct for \( E > 10 \text{ meV} \) electrons, in order to increase the signal-to-noise ratio.

Mass spectra of internal energy selected parent ions can thus be obtained as a function of the photon energy. The initial internal energy distribution of the neutral molecule is transposed onto the ion manifold by the photon energy less the adiabatic ionization energy \( (I_{\text{ad}}) \) thanks to mostly constant Franck–Condon factors for sequence transitions [38]. If the dissociative photoionization is not prompt on the time scale of the experiment \((k < 10^{7} \text{ s}^{-1})\), only daughter ions formed in the first 100 ns after ionization will contribute to the mass spectrum at the TOF of the daughter ion. Those that are formed while the parents are still residence times in the acceleration region can be several \( \mu \text{s} \), dissociative photoionization rate constants can be directly measured in the \( 10^{4} \text{ s}^{-1} < k < 10^{9} \text{ s}^{-1} \) range. Urea daughter ion peaks were symmetric at all energies, indicating fast dissociations and an absence of a kinetic shift [52,53].

In a first, fast photo dissociation step \((k > 10^{7} \text{ s}^{-1})\), all parent ions with more internal energy than the barrier height, \( E_0 < I_{\text{ad}} \), will form daughter ions. Fractional parent and daughter ion abundances are plotted as a function of the photon energy in the breakdown diagram. As a consequence, the \( T = 0 \text{ K} \) onset, \( E_0 \), can be determined as the photon energy, at which all parent ions have enough internal energy to dissociate, in other words at the disappearance energy of the parent ion in the breakdown diagram. For a consecutive, second dissociative photoionization reaction, the fractional ion abundances of the first and second daughter ions are determined by the relative rate constants, which are modelled by statistical rate theories.
3. Results and discussion

3.1. Dissociative photoionization of urea

Threshold photoionization mass spectra were taken in the 10.25 to 14.25 eV photon energy range. In addition to the parent ion (CO(NH2)2+, m/z = 60), we also observed the ammonia (NH3+ m/z = 17) and protonated isocyanic acid (H2NCO+, m/z = 44) fragment ions, indicating the following dissociative photoionization processes:

\[
\begin{align*}
\text{CO(NH2)2} + h\nu &\rightarrow \text{NH3}^+ + \text{HNCO} + e^- , \quad (1) \\
\text{CO(NH2)2} + h\nu &\rightarrow \text{H2NCO}^- + \text{NH}_2 + e^- . \quad (2)
\end{align*}
\]

The corresponding peaks in the mass spectra are integrated and the fractional ion abundances are plotted as a function of the photon energy in the breakdown diagram (Figure 1). Since the TOF peak shapes are symmetric, the dissociation reactions are fast on the time scale of the experiment (k > 10^7 s^-1), and the onset energies can be derived by modelling only the breakdown diagram.

The observation that the parent ion is not metastable even though its potential energy well is approximately 1 eV (100 kJ mol^-1), indicates that the onset energy corresponds to the dissociative photoionization energy and not to an isomerization barrier for H transfer with a tight transition state, and across which slow tunnelling rates would be observable. The break- down diagram of such a fast dissociation can be modelled by the cumulative distribution function of the neutral internal energy distribution.

\[
BD(h\nu) = \frac{1}{k} \int_{E_0}^{E} P_0(E, h\nu) dE = \frac{1}{\hbar} \int_{E_0}^{-h\nu} P_\infty(E) dE ,
\]

where \(BD(h\nu)\) is the fractional parent ion abundance at photon energy \(h\nu\), \(E_0\) is the dissociative photoionization onset at \(T = 0\) K, and \(P\) is the normalized internal energy distribution for the parent ion (\(P_0\)) and the neutral (\(P_\infty\)). The neutral internal energy distribution is obtained by normalizing the Boltzmann distribution \(\rho(E) \propto e^{-E/kT}\), in which \(ab\ initio\) rotational constants and harmonic vibrational frequencies are used to calculate the density of states, \(\rho(E)\). The integral in equation (3) vanishes at \(h\nu = E_0\), in other words the onset energy is given by the disappearance energy of the parent ion [55]. The inset in Figure 1 shows the fitted \(E_0(\text{NH}_3^+ + \text{HNCO}) = (10.838 \pm 0.010)\) eV, at a fitting temperature of 50 °C, indicating some cooling after the oven source. This can be converted to a \(T = 0\) K reaction energy for the reaction

\[
\text{CO(NH2)2} \rightarrow \text{NH}_3 + \text{HNCO} , \quad \Delta H_0^\circ = 62.9 \pm 1.0 \text{ kJ mol}^{-1}
\]

by subtracting the ammonia ionization energy, 10.186 eV [34]. The most recent urea enthalpy of formation at \(T = 298\) K can be converted to \(\Delta H_0^\circ = 221.3\) kJ mol^-1 and used with the 0 K enthalpies of formation of \(\text{NH}_3\) and \(\text{HNCO}\) (Table 1) to calculate the reaction energy predicted by literature values for (4) as \(\Delta H_0^\circ\). Evidently, this does not agree with the measurement reported here. The fact that the measured onset is lower than the literature value, however, is the second reassuring sign that the H-migration transition state lies no higher in energy than the dissociative photoionization products. On the other hand, there is no experimental indication as to whether the urea or the isocyanic acid enthalpy of formation is in error.

To shed light on the discrepancy in the reaction energy of (4), we consider the second, parallel dissociative photoionization channel (2), which produces \(\text{H}_2\text{NCO}\) and \(\text{NH}_3\). The isocyanic acid proton affinity, a quantity easy to calculate accurately [56], and the amidogen (\(\text{NH}_2\)) enthalpy of formation, \(\Delta H_0^\circ(\text{NH}_2, 0 K, g) = (188.9 \pm 0.2)\) kJ mol^-1 [24], link the second onset to the first one. The fractional daughter ion abundances in the 11.4 eV to 14 eV photon energy range are determined by the relative rate constants of the two dissociative photoionization processes (1) and (2). Normalized, the dissociation rate of the second reaction is much lower at the onset than that of the lower lying channel at the same energy, which makes an extrapolation step necessary in order to determine the second onset. A rate curve \(k_2(E)\) is obtained for the lower energy channel either based on direct rate information, when available, or else calculated using statistical theory and \(ab\ initio\) computations. Then, the rate curve for the second channel, \(k_2(E)\), is fitted to reproduce the measured fractional abundances and extrapolated to the onset [38]. Different statistical approaches, such as RAC-RRKM (rigid activated complex Rice–Ramsperger–Kassel–Marcus model) or SSACM (simplified statistical adiabatic channel model), which can be conveniently derived from PST (phase space theory) differ in how they describe the bottleneck between the reactant and products in phase space, i.e., the transition state [38]. Ionic dissociations typically occur along purely attractive potentials with loose transition states. In RRKM, a transition state is defined by constraining the reaction coordinate, typically a bond length, at 0.4 nm to 0.5 nm. Harmonic vibrational frequencies are then used to obtain a first guess for the transition state number of states, \(\tilde{N}(E - E_0)\), the only adjustable parameter in the rate equation

\[
k(E) = \frac{\sigma \tilde{N}(E - E_0)}{\hbar \rho(E)} ,
\]

where \(\rho\) is the density of states of the dissociating ion, approximated in this case with that of the urea cation, \(h\) Planck’s constant and \(\sigma\) the symmetry number [57]. The density of states of the dissociating ion is referenced to the ion ground state, which is how the adiabatic ionization energy of urea appears in the model. Instead of previous literature values, not supported by Franck–Condon analyses, we used the average G3, G3B3, CBS-QB3 and CBS-APNO calculated \(E_{\text{irr}} = 9.83\) eV. The transition state number of states can be fitted by scaling the translational mode vibrational frequencies by an adjustable parameter [38]. However, the assumption of a rigid transition state is not strictly applicable for loose transition states [58]. Indeed, similarly to recent findings on the second, methyl loss channel in the dissociative photoionization of ethanol [54], we were unable to fit the onset of \(\text{NH}_3\) loss with RRKM rate curves. In the SSACM model [59], the fitting parameter is \(c\) in the rigidity factor expression. In this study,
is used to scale PST rates and characterizes a transition state shift to lower reaction coordinate values as the energy is increased. The parent ion is not metastable at the threshold of HNCO loss, which means that all c values are acceptable which lead to dissociation rates no smaller than $10^7$ s$^{-1}$ at the threshold for (1). As a consequence, the rate curve for the second dissociation is flexible and by simultaneously fitting the rigidity factor for both dissociation reactions, the breakdown diagram can be fitted in a 35 kJ mol$^{-1}$ window for the second $E_0$ and the second onset cannot be used to confirm the ca. 5 kJ mol$^{-1}$ discrepancy between the literature based and the herein derived reaction energy for (4). Reactions (1) and (2) are nevertheless established as the dissociative photoionization reaction instead: the Horb–O–C bond angle and the Horb–O–C–N dihedral angle. The potential energy surfaces (PES) were generated by plotting the energies of the optimized structures with respect to the initial spherical coordinates of the hydrogen atom (figure 3). Points are omitted, at which either the electronic wave function or the geometry optimization did not converge. The hydrogen atom can move around the molecule or the ion along trajectories on these surfaces.

The energy scale in the inclined images for the neutral and ionic urea PES in figure 3 is 0–4 eV (ca. 0 to 400 kJ mol$^{-1}$) in order to enable their direct comparison. The maximum energy in the top view is adjusted to 1 eV in the ion, figure 3(a) and 2 eV in the neutral, figure 3(c), to emphasize the features of each surface. Three major domains can be discerned: first, the $-90^\circ < \phi < 30^\circ$, $60^\circ < \theta < 120^\circ$ minimum energy region corresponds to the global (NH$_2$)$_2$C=O structure minimum. Second, at higher $\phi$ values the hydrogen atom moves over a 1.5 eV barrier in the neutral and about 1 eV in the ion, the N–H bond breaks and an O–H bond is formed to make isourea. The ellipse shaped minimum describes the OH group internal rotation in the molecule. The transition structure at $\phi = 90^\circ$, $\theta = 90^\circ$ describes flipping over the H atom over the oxygen. Third, at $\phi < -120^\circ$, $\theta$ hardly plays a role, and the 0.5 eV (48 kJ mol$^{-1}$) structures correspond to NH$_3$ loss from the molecule, i.e., the thermolysis products of urea, ammonia and isocyanic acid. The barriers for H transfer to O and H transfer to N leading the NH$_3$ loss are comparable in the neutral. Both, especially the latter, are much smaller in the ion. Bernhard et al. proposed that the activation energy for urea thermolysis is 90 kJ mol$^{-1}$ even on a TiO$_2$ catalyst [64] at a reaction energy of (62.9 ± 1.0) kJ mol$^{-1}$ (vide supra). Using 9.83 eV as urea ionization energy together with the measured onset energy for reaction (1), the CO(NH$_2$)$_2$ + $\rightarrow$ NH$_3$ + + HNCO loss dissociation energy in the ion is 97 kJ mol$^{-1}$, i.e., more endothermic than in the neutral, whereas the isomerization barrier is smaller in the ion. This explains why dissociative photoionization takes place without a reverse barrier even without a catalyst.

3.2. Hydrogen atom hopping mechanism

Hydrogen atom migration occurs in urea thermolysis as well as in its dissociative photoionization. The following approach was used to confirm that the barrier to H-shift in the ion is lower than the dissociation energy. The H atom can migrate to the neighbouring nitrogen or to the oxygen atom. As a consequence, a comprehensive picture of the roaming H atom can only be obtained from at least a two-dimensional potential energy surface. Above a certain threshold, hydrogen atoms probably orbit the molecule or ion core in a somewhat delocalized fashion, analogously to the Horb atom in a somewhat delocalized fashion, analogously to the Horb–O–C bond angle and the Horb–O–C–N dihedral angle. The potential energy surfaces (PES) were generated by plotting the energies of the optimized structures with respect to the initial spherical coordinates of the hydrogen atom (figure 3). Points are omitted, at which either the electronic wave function or the geometry optimization did not converge. The hydrogen atom can move around the molecule or the ion along trajectories on these surfaces.

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3.3. Ab initio reaction energies

The $T = 0$ K appearance energy of NH$_3$ + in urea is a direct measurement of the CO(NH$_2$)$_2$ + $\rightarrow$ HNCO + NH$_3$ + dissociative photoioni-
zation reaction energy at $T = 0$ K, and, using the ionization energy of ammonia, an indirect measure for the CO(NH$_2$)$_2$ → HNCO + NH$_3$ reaction enthalpy. As discussed previously, the ammonia thermochemistry is very well established. On the other hand, there is significant scatter in the urea sublimation enthalpy [9,11,12], and it has only been a gradually formed view that the measured isocyanic acid dissociation threshold corresponds to the dissociation energy and not only to its lower limit [27–30], yielding the isocyanic acid enthalpy of formation. The dissociative photoionization energy of urea reported here can be converted to yield the neutral dissociation energy, and it confirms more recent thermochemical measurements over the older ones. However, it also suggests that the urea or the isocyanic acid enthalpies of formation may be in error, or at least have been assigned overly optimistic uncertainties. Unfortunately, no experimental information is available as to which quantity needs to be revised. Furthermore, errors of the same sign cancel out when calculating the reaction energy. Thus, a suitable experimental anchor is missing to the absolute scale of enthalpies of formation.

Ab initio isodesmic and isoelectronic reaction energy calculations were carried out using Gaussian09 [61] to remedy this with the help of ancillary enthalpies of formation listed in table 1. Isodesmic reaction energy calculations are often accurate to around 1 kJ mol$^{-1}$, whereas isoelectronic reaction energies are slightly less reliable [65,66].

The calculated gas phase thermal enthalpies at $T = 298$ K are generally considered to be exact, and are reported at the W1 level.

FIGURE 3. Potential energy surfaces for an H atom roaming around the urea (a) cation and (c) neutral core. The inclined views are plotted between 0 eV and 4 eV for easy comparison, the top views have energy scales of (a) 0–1 and (c) 0–2 eV with the zero level corresponding to the global minimum. (b) Sample structures from the potential energy surfaces.
for urea and isocyanic acid in Table 1. The differences between the W1 and CBS-APNO thermal enthalpies for urea and isocyanic acid were 0.17 and 0.02 kJ·mol⁻¹, respectively. Internal hindered rotors, particularly with low rotational barriers, such as methyl groups in radicals can lead to room temperature corrections to the harmonic oscillator approximation on the order of 1 kJ·mol⁻¹ [41]. Since the harmonic frequency corresponding to NH₂ rotation in urea is about 400 cm⁻¹, the internal hindered rotor correction is negligible, on the order of 0.00 to 0.16 kJ·mol⁻¹, depending on the model [67,68].

The urea enthalpy of formation was addressed by calculating an isodesmic reaction energy based on CH₂NH₂ and CO₂, as well as two reaction energies based on NH₃ and CO₂, and CH₄, N₂ and H₂O with the CBS-APNO [69] and W1 [70,71] model chemistry:

\[
4\text{CH}_2\text{NH}_2 + \text{CO}_2 \rightarrow 2\text{CO(NH}_2)_2 + 3\text{CH}_4,
\]

\[
2\text{NH}_3 + \text{CO} \rightarrow \text{CO(NH}_2)_2 + \text{H}_2\text{O},
\]

\[
\text{CH}_4 + \frac{1}{2}\text{N}_2 + \text{H}_2\text{O} \rightarrow \text{CO(NH}_2)_2 + \frac{1}{2}\text{H}_2.
\]

Reaction energy calculations involving isocyanic acid are hampered by the lack of suitable anchor compounds. The isoelectronic reaction

\[
\text{NH}_3 + \text{CO}_2 \rightarrow \text{HNCO} + \text{H}_2\text{O}.
\]

as well as the reaction

\[
\text{CH}_4 + 0.5\text{N}_2 + \text{H}_2\text{O} \rightarrow \text{HNCO} + 0.5\text{H}_2.
\]

analogous to (7c) have been evaluated. The computed W1 reaction energies are listed in Table 2 together with the differences to CBS-APNO results.

The measured dissociative photoionization energy and the computed reaction energies can now be used in concert to arrive at revised gas phase enthalpies of formation of both isocyanic acid and urea.

3.4. Thermochemistry

The iPEPICO experiment indicates a 5.1 kJ·mol⁻¹ discrepancy when compared with the latest published enthalpies of formation for urea and isocyanic acid. Using previously published and still widely used enthalpies of formation, the disagreement increases to more than 20 kJ·mol⁻¹. As discussed previously, ab initio results can help anchor the enthalpies of formation in question to the absolute scale and decide which needs to be revised. Computational and experimental results are analyzed simultaneously with an error function, which compares enthalpy of formation based reaction energies with measured and computed values,

\[
E = \frac{(\Delta H_{\text{W1}} - \Delta H_{\text{CBS-APNO}})^2}{\Delta H_{\text{W1}} - \Delta H_{\text{CBS-APNO}}} \cdot \text{mol}^{-1}.
\]

The error function was minimized by relaxing the urea and isocyanic acid enthalpies of formation. The first term in the error function had a starting value of 16.1, with a minimum at 16.0, when both enthalpies of formation were shifted by the same amount of –0.1 kJ·mol⁻¹. The small change indicates good anchoring of the average enthalpies of formation to the absolute scale. The first, computational term in (9) decreased further to 6.48 with the experimental term at 1.94 when the urea and isocyanic acid enthalpies of formation were optimized independently. The derived corrections are 2.43 kJ·mol⁻¹ to the urea and –1.54 kJ·mol⁻¹ to the isocyanic acid enthalpy of formation. The revised values are listed in Table 1. The uncertainties are evaluated for both enthalpies of formation based on three terms: (1) the experimental uncertainty, 1.0 kJ·mol⁻¹, (2) the ab initio uncertainty of the corrections, 1 kJ·mol⁻¹ and (3) the uncertainty in the thermal enthalpies, 0.2 kJ·mol⁻¹. The overall error bar of 1.4 kJ·mol⁻¹ indicates that both the urea and the isocyanic acid enthalpies of formation are revised significantly. However, our isocyanic acid results agree with the earlier value of Zyrionov et al. [28] and with the focal point analysis of Schuurman et al. [32], and the results for urea confirm the value in the NIST Chemistry Webbook [13].

### Table 1
Ancillary and derived thermochemical data.

| Reaction | \( \Delta H_{\text{ref}}(\text{g})/\text{(kJ mol}^{-1}\text{)} \) | \( \Delta H_{\text{ref}}(\text{g})/\text{(kJ mol}^{-1}\text{)} \)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_3 )</td>
<td>–38.57 ±0.03</td>
<td>Ref. [24]</td>
</tr>
<tr>
<td>( \text{NH}_2 )</td>
<td>188.9 ±0.2</td>
<td></td>
</tr>
<tr>
<td>( \text{NH} )</td>
<td>358.7 ±0.2</td>
<td></td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>–113.81 ±0.03</td>
<td></td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>–303.108 ±0.014</td>
<td></td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>–66.56 ±0.06</td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>–238.918 ±0.027</td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>8.47</td>
<td>Ref. [18]</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>8.68</td>
<td></td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>8.67</td>
<td></td>
</tr>
<tr>
<td>( \text{C(s)} )</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>( \text{CH}_2\text{NH}_2 )</td>
<td>–7.0 ±1.5</td>
<td>Ref. [65]</td>
</tr>
<tr>
<td>( \text{HNCO} )</td>
<td>–114.7 ±0.4</td>
<td>See Introduction for references</td>
</tr>
<tr>
<td>( \text{CO(NH}_2)_2 )</td>
<td>–221.3 ±0.4</td>
<td></td>
</tr>
<tr>
<td>( \text{HNCO} )</td>
<td>–116.2 ±1.4</td>
<td></td>
</tr>
<tr>
<td>( \text{CO(NH}_2)_2 )</td>
<td>–219.9 ±1.4</td>
<td></td>
</tr>
</tbody>
</table>

Converts to \( T = 0 \text{ K from } -238.1 \text{ kJ mol}^{-1} \) at \( T = 298 \text{ K using the W1 thermal enthalpy.} \)

\( a \) Converts to \( -119.2 \text{ kJ mol}^{-1} \) at \( T = 298 \text{ K.} \)

\( b \) Converts to \( -235.7 \text{ kJ mol}^{-1} \) at \( T = 298 \text{ K.} \)

\( c \) Updated values are listed in Table 1. The uncertainties are evaluated from the experimental term at 1.94 when the urea and isocyanic acid enthalpies of formation were optimized independently.

\( d \) The first, computational term in (9) decreased further to 6.48 with the experimental term at 1.94 when the urea and isocyanic acid enthalpies of formation were optimized independently. The derived corrections are 2.43 kJ·mol⁻¹ to the urea and –1.54 kJ·mol⁻¹ to the isocyanic acid enthalpy of formation.

\( e \) The first, computational term in (9) decreased further to 6.48 with the experimental term at 1.94 when the urea and isocyanic acid enthalpies of formation were optimized independently. The derived corrections are 2.43 kJ·mol⁻¹ to the urea and –1.54 kJ·mol⁻¹ to the isocyanic acid enthalpy of formation.

\( f \) The overall error bar of 1.4 kJ·mol⁻¹ indicates that both the urea and the isocyanic acid enthalpies of formation are revised significantly. However, our isocyanic acid results agree with the earlier value of Zyrionov et al. [28] and with the focal point analysis of Schuurman et al. [32], and the results for urea confirm the value in the NIST Chemistry Webbook [13].

### Table 2
Computed and measured reaction energies at \( T = 0 \text{ K.} \)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>This work(^a)</th>
<th>Uncert.(^b)</th>
<th>Literature</th>
<th>Revised(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4\text{CH}_2\text{NH}_2 + \text{CO}_2 \rightarrow 2\text{CO(NH}_2)_2 + 3\text{CH}_4 )</td>
<td>–214.77</td>
<td>2.56(^d)</td>
<td>–221.2</td>
<td>–216.37</td>
</tr>
<tr>
<td>( 2\text{NH}_3 + \text{CO} \rightarrow \text{CO(NH}_2)_2 + \text{H}_2\text{O} )</td>
<td>12.02</td>
<td>3.33</td>
<td>10.03</td>
<td>12.43</td>
</tr>
<tr>
<td>( \text{CH}_4 + \frac{1}{2}\text{N}_2 + \text{H}_2\text{O} \rightarrow \text{CO(NH}_2)_2 + \frac{1}{2}\text{H}_2 )</td>
<td>85.41</td>
<td>0.35</td>
<td>84.18</td>
<td>86.58</td>
</tr>
<tr>
<td>( \text{NH}_3 + \text{CO}_2 \rightarrow \text{HNCO} + \text{H}_2\text{O} )</td>
<td>77.01</td>
<td>0.16</td>
<td>78.06</td>
<td>76.56</td>
</tr>
<tr>
<td>( \text{CH}_4 + \frac{1}{2}\text{N}_2 + \text{H}_2\text{O} \rightarrow \text{HNCO} + 2\frac{1}{2}\text{H}_2 )</td>
<td>191.17</td>
<td>6.85</td>
<td>190.78</td>
<td>189.28</td>
</tr>
<tr>
<td>( \text{CO(NH}_2)_2 \rightarrow \text{HNCO} )</td>
<td>62.9</td>
<td>1.0</td>
<td>68.0</td>
<td>64.0</td>
</tr>
</tbody>
</table>

\( a \) W1 computed reaction energies and the measured dissociative photoionization threshold converted to neutral state with the known ammonia \( E_{\text{el}}. \)

\( b \) The absolute reaction energy difference between CBS-APNO and W1 results and the measurement uncertainty are listed.

\( c \) Based on the revised isocyanic acid and urea heats of formation from.

\( d \) Normalized for one mole urea.
4. Conclusions

Imaging photoelectron photoion coincidence was used to establish the threshold for the lowest energy dissociative photoionization channel of urea leading to isocyanic acid and ammonia. This process is related to the thermochemistry of urea pyrolysis, a crucial step in the selective catalytic reduction of NOx emissions in diesel vehicles.

The second dissociative photoionization channel is the loss of NH$_2$ to make H$_2$NCO$^-$, protonated isocyanic acid. The relative rates could not be modelled with an RRKM approach, underlining the shortcomings of RRKM when describing reactions with loose transition states. The SSACM model provided an adequate fit, which confirmed the dissociative photoionization mechanism, but the error limits of the threshold energy were too big to be useful in narrowing the uncertainties.

Isocyanic acid production from urea supposes hydrogen atom migration, and H roaming around the molecular core was studied with density functional theory in urea and the urea cation. The potential energy surface showed three minimum ranges, one corresponding to NH$_2$ internal rotation in urea, one to OH internal rotation in isourea as well as a marked decrease in H-transfer barrier in the ion all imply that the measured onset for the first step corresponds to the dissociation photoionization reaction energy and not to an isomerization barrier.

The difference between the experimental onset for isocyanic acid production and the one based on the latest literature enthalpies of formation was found to be 5.1 kJ mol$^{-1}$, more than four times the combined uncertainty range of the two values. The discrepancy increases to $>$20 kJ mol$^{-1}$ when previously published, and still widely used thermochemical values are employed. Computed reaction energies implied a minor correction to the average enthalpy of formation of urea and isocyanic acid, and suggested an increase to the urea and a decrease to the isocyanic acid enthalpies of formation to make thermochemical data agree with the experimental results. Thus, the room temperature enthalpy of formation of urea is confirmed at $-235.7 \pm 1.4$ kJ mol$^{-1}$, whereas that of isocyanic acid is established at $-119.2 \pm 1.4$ kJ mol$^{-1}$, corresponding to $-116.2 \pm 1.4$ kJ mol$^{-1}$ at $T = 0$ K.

Acknowledgement

We are grateful to Drs. Daniel Peitl and Oliver Kröcher for discussions regarding SCR. The experimental work reported was carried out at the UUV Beamline of the Swiss Light Source, Paul Scherrer Institut.

References

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