



Research paper

Gas-phase standard enthalpies of formation of urea-derived compounds: A quantum-chemical study



Dennis Gratzfeld, Matthias Olzmann*

Institut für Physikalische Chemie, Karlsruher Institut für Technologie (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

ARTICLE INFO

Article history:

Received 27 March 2017
 In final form 2 May 2017
 Available online 5 May 2017

Keywords:

Enthalpies of formation
 Ureas
 Triazines
 Methanimine
 Methylamine
 Explicitly correlated coupled-cluster theory
 HEAT protocol

ABSTRACT

Gas-phase standard enthalpies of formation of selected ureas and *s*-triazines were calculated at the CCSD (F12*)/cc-pVTZ-F12// ω B97X-D/cc-pVTZ level of theory by employing isodesmic reactions. The following values were obtained ($T = 298.15$ K, units: kJ mol^{-1} , estimated confidence interval 95%): urea, -231.9 ± 2.8 ; biuret, -430.0 ± 4.5 ; triuret, -620.3 ± 6.3 ; cyanuric acid, -451.6 ± 6.3 ; ammeline, -303.9 ± 6.4 ; ammeline, -106.5 ± 6.2 ; melamine, 70.1 ± 7.0 . The standard enthalpies of formation of methanimine and methylamine, which were required for the isodesmic reactions, were calculated from atomization reactions by using several variants of the HEAT approach. The following results were considered most reliable ($T = 298.15$ K, units: kJ mol^{-1} , estimated confidence interval 95%): methanimine, 89.0 ± 1.0 ; methylamine, -20.7 ± 1.0 .

© 2017 Published by Elsevier B.V.

1. Introduction

Urea and urea-derived compounds play a crucial role in both biological systems and industrial processes. Among technical applications, the urea-based exhaust after treatment in mobile combustion devices is particularly noteworthy. In this so-called urea selective catalytic reduction (Urea-SCR) process (see e.g. [1,2]), NO_x emissions from lean-burn combustion devices such as diesel engines are catalytically reduced to N_2 by ammonia that is produced in situ from injected urea-water solution. The thermal decomposition and hydrolysis of urea under these conditions essentially yields ammonia and carbon dioxide, but condensation products of urea like biuret, triuret, cyanuric acid, ammeline, ammeline, and melamine are also formed [1] (for structures see Scheme 1). These unwanted byproducts generate deposits and may mechanically block the exhaust gas system but also reduce the efficiency of the NO_x reduction catalyst.

To understand and model the formation of these compounds, their kinetic and thermodynamic data have to be known. Unfortunately, information on these quantities in the literature is scarce, and experimental or calculated values, if available, exhibit considerable scatter. Even enthalpies of formation as the most fundamental quantities in any thermodynamic and kinetic model are inconsistent for some of the above-mentioned species and, to the

best of our knowledge, are actually missing for three of them (triuret, ammeline, and ammeline).

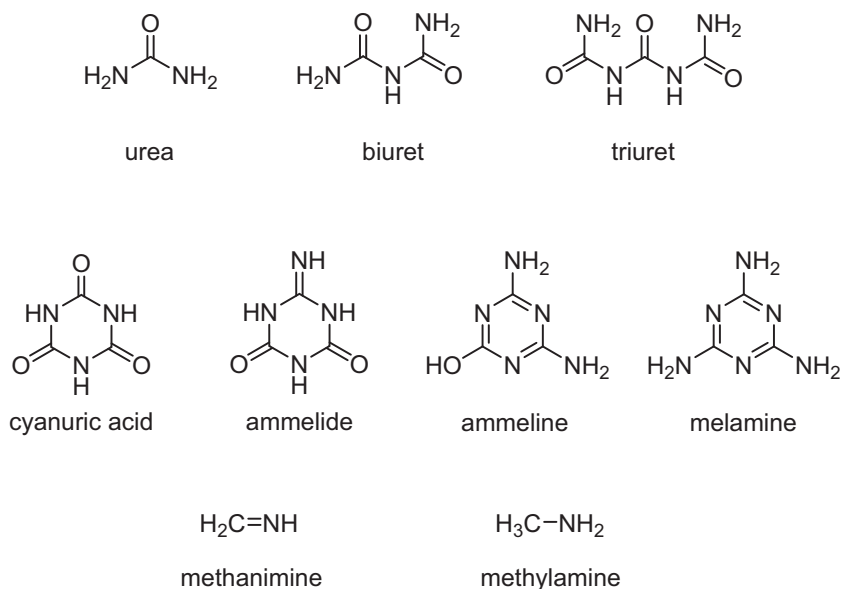
To complete and improve this data set and to assess the quality of the available literature values, we performed high-level quantum-chemical calculations to determine the gas-phase standard enthalpies of formation of these compounds. We used the approach via isodesmic reactions [3] to exploit error compensation and combined well-known, recommended standard enthalpies of formation of reactants and products with calculated values for the standard enthalpies of reaction. For these calculations, coupled-cluster theory [4] was used to obtain single-point electronic energies at reactant and product geometries optimized with density-functional theory (DFT) [5].

To construct adequate isodesmic reactions, the concept of bond separation reactions (BSR) was applied [3,6]. Here, due to missing data and for the sake of consistency, it turned out appropriate to separately calculate the standard enthalpies of formation of methanimine and methylamine (for structures, see also Scheme 1), which both are constituents of the BSR. For these two species, the so-called HEAT protocol [7–9] was applied, which is a specially designed quantum-chemical composite method to achieve high accuracy for standard enthalpies of formation. The HEAT protocol is known to often yield sub- kJ mol^{-1} accuracy for the enthalpies of formation of small stable molecules [9,10].

The gas-phase standard enthalpies of formation calculated in the present work can serve as a consistent basis to obtain values for other nitrogen-containing compounds, e.g. through

* Corresponding author.

E-mail address: matthias.olzmann@kit.edu (M. Olzmann).

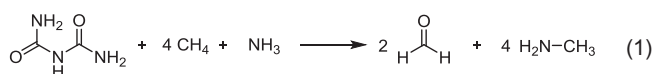


Scheme 1.

group-additivity methods. They can also be used to model possible gas-phase contributions to the Urea-SCR process [11,12], or they can be taken as a starting point to estimate or calculate the technically relevant condensed-phase values.

2. Theoretical methods

As already mentioned in the introduction section, the standard enthalpies of formation were calculated by employing isodesmic reactions. As a straightforward method for constructing adequate isodesmic reactions, the concept of BSR [3,6] was applied. BSR are defined as reactions in which “the molecule is separated into its simplest parents containing the same component bonds” [6]. Eq. (1) exemplarily shows the BSR employed for biuret, and a complete list of the BSR is given in [Scheme S2 of the Supplementary Material](#).



The geometries and harmonic vibrational frequencies of all compounds occurring in the isodesmic reactions were calculated with DFT at the $\omega\text{B97X-D/cc-pVTZ}$ level of theory [13,14] by using the Gaussian 09 program package [15]. For comparison the geometry of urea was additionally optimized at the CCSD(T)/cc-pVTZ level of theory by using the MOLPRO 2012 program suite [16]. The differences will be discussed below.

The electronic-energy contributions were calculated at the $\text{CCSD(F12*)/cc-pVTZ-F12}$ level of theory [17–19] with the TURBO-MOLE 7.0 package of programs [20]. Both vibrational frequencies and zero-point vibrational energies were multiplied with the same scaling factor, f , from the Computational Chemistry Comparison and Benchmark Database (CCCBDB) [21] ($\omega\text{B97X-D/cc-pVTZ}$: $f = 0.956$, CCSD(T)/cc-pVTZ : $f = 0.975$). The geometries, zero-point vibrational energies, and electronic energies of all the species involved are listed in the [Supplementary Material](#), and also geometries and energies of different tautomers of the triazines are given there. For the calculation of the standard enthalpies of formation,

only the most stable tautomers, shown in [Scheme 1](#), were considered.

The gas-phase standard enthalpies of formation of the reference species except those of methylamine (CH_3NH_2) and methanimine (CH_2NH), were taken from the Active Thermochemical Tables (ATcT) [22,23], where the following values at $T = 298.15 \text{ K}$ were listed: (-74.533 ± 0.057) kJ mol^{-1} for CH_4 , (-45.561 ± 0.03) kJ mol^{-1} for NH_3 , (-109.15 ± 0.11) kJ mol^{-1} for HCHO , (-200.72 ± 0.17) kJ mol^{-1} for CH_3OH , (88.70 ± 0.98) kJ mol^{-1} for CH_2NH , and (-20.91 ± 0.53) kJ mol^{-1} for CH_3NH_2 . Because the values for CH_2NH and CH_3NH_2 exhibit the largest uncertainty, we additionally calculated these standard enthalpies of formation by using different variants of the HEAT protocol [7–9].

In all HEAT protocols, the total ground-state energy of a molecule is given by

$$E_{\text{HEAT}} = E_{\text{HF}}^{\infty} + \Delta E_{\text{CCSD(T)}}^{\infty} + \Delta E_{\text{CCSDT}} + \Delta E_{\text{HLC}} + \Delta E_{\text{rel}} + \Delta E_{\text{SO}} + \Delta E_{\text{DBOC}} + \Delta E_{\text{ZPE}} \quad (2)$$

where E_{HF}^{∞} is the Hartree-Fock energy, and $\Delta E_{\text{CCSD(T)}}^{\infty}$ is the CCSD (T) correlation energy, and both quantities are extrapolated to the basis-set limit. The terms ΔE_{CCSDT} and ΔE_{HLC} account for higher-level electron correlation, ΔE_{rel} is the scalar relativistic contribution, ΔE_{SO} is the difference between the ground-state energy and the weighted average of spin-orbit levels, ΔE_{DBOC} is the diagonal Born-Oppenheimer correction, and ΔE_{ZPE} is the correction of zero-point vibrational energy including anharmonicity. These anharmonicity contributions are based on second-order vibrational perturbation theory (VPT2) and were calculated by using the $\text{CCSD(T)(full)/cc-pVQZ}$ quartic force field. All geometries used in the HEAT protocols were optimized at the $\text{CCSD(T)(full)/cc-pVQZ}$ level of theory.

In the actual calculations of the current work, two minor modifications were made to the original HEAT protocol: First, instead of using calculated values for the ΔE_{SO} contribution, the experimental values given in the CCCBDB [21] were adopted, and, second, as recommended in Ref. [9], the diagonal Born-Oppenheimer correction, ΔE_{DBOC} , was calculated at the CCSD/aug-cc-pCVQZ [24,25] level instead of using the HF/aug-cc-pVTZ level. The numerical values of the terms in Eq. (2) for methanimine and methylamine are listed in [Table S2 of the Supplementary Material](#).

Download English Version:

<https://daneshyari.com/en/article/5378073>

Download Persian Version:

<https://daneshyari.com/article/5378073>

[Daneshyari.com](https://daneshyari.com)