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Proton Affinities and Heats of Formation of the Imines CH_2=NH, CH_2=NMe and PhCH=NH

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The proton affinities of the imines CH_2=NH, CH_2=NMe and PhCH=NH have been determined by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry to be 854 ± 8 kJ mol^{-1}, 880 ± 8 kJ mol^{-1} and 908 ± 8 kJ mol^{-1}, respectively. These results lead, in conjunction with known ΔH_f° values for the protonated species, to $\Delta H_f^\circ(CH_2{=}NH) = 69 \pm 8$ kJ mol^{-1}, which is significantly lower than previously reported in the literature, and to $\Delta H_f^\circ(CH_2{=}NMe) = 44 \pm 8$ kJ mol^{-1}. The proton affinities of the small imines are between the values for the corresponding amines and nitriles. The decrease in proton affinity with the change in hybridization of the nitrogen atom from sp^3 to sp^2 to sp is discussed together with the increase in proton affinity upon introduction of a methyl group on either the carbon atom or the nitrogen atom in CH_2=NH.

The basicity of a species is known to depend upon the hybridization of the atom that binds the proton as illustrated by the decrease in proton affinity (E_{pa})[†] down the series $H_3C{-}CH_2^-$ (1758 kJ mol^{-1}),[1] $H_2C{=}CH^-$ (1705 kJ mol^{-1})[1] and $HC{\equiv}C^-$ (1576 kJ mol^{-1}).[2] A similar trend is observed for nitrogen-containing compounds since the reported E_{pa} values for amines are much higher than those for nitriles.[3] Reliable proton affinities of the intermediate imines, however, are nearly absent from the literature. Experiments[4] and *ab initio* calculations[5–11] suggest that the E_{pa} value for the simplest imine, CH_2=NH, is about 40 kJ mol^{-1} lower than the value for $MeNH_2$. The decrease in E_{pa} on going from $MeCH_2NH_2$ to MeCH=NH is reported to be 11 kJ mol^{-1} only,[12,13] providing evidence that introduction of a methyl group on the carbon atom in CH_2=NH partly compensates the hybridization effect. We have determined the E_{pa} values of selected imines by means of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry[14–18] in order to obtain a more consistent view on the dependence of the E_{pa} of amines, imines and nitriles upon the hybridization of the nitrogen atom and upon substitution of a hydrogen atom for a methyl group.

Imines with hydrogen atoms or small alkyl groups attached to the carbon or the nitrogen atom are known to be unstable in the condensed phase as exemplified by CH_2=NH, which undergoes a rapid condensation reaction at temperatures above −80 °C.[19] This precludes straightforward introduction of the neutral imines into FT-ICR instruments and hampers determination of the proton affinities of the simplest imines by studying equilibria with reference bases of known basicity. By contrast, immonium ions are easily formed in the gas phase by α-cleavage of amine radical cations[20] as shown in eqns. (1)–(3)

$$RCH_2NH_2^{\cdot +} \longrightarrow CH_2{=}NH_2^{+} + R^{\cdot} \qquad (1)$$

$$RCH_2NHMe^{\cdot +} \longrightarrow CH_2{=}NHMe^{+} + R^{\cdot} \qquad (2)$$

$$PhCHRNH_2^{\cdot +} \longrightarrow PhCH{=}NH_2^{+} + R^{\cdot} \qquad (3)$$

$$(R = H, Me, Et)$$

for systems studied here. Subsequently the proton affinities of the imines can be obtained from the occurrence/non-occurrence of proton transfer in the reactions of the immonium ions with various bases, provided that the reactions are carried out under conditions where an exothermic proton transfer will occur whereas an endothermic process will not take place.

Table 1 Results of reactions between immonium ions and reference bases[a]

RH^+	Base	E_{pa}[b]/ kJ mol^{-1}	Proton transfer
$CH_2{=}NH_2^+$	Pyrrole	868	+
	Diisopropyl ether	862	+
	Ammonia	853.5	±
	Styrene	845	−
	Diethyl ether	838	−
$CH_2{=}NHMe^+$	Methylamine	896	+
	Dimethyl sulphoxide	884	+
	Aniline	876	−
	Pyrrole	868	−
$PhCH{=}NH_2^+$	2,2-Dimethylpropylamine	918	+
	Isopropylamine	915	+
	Benzylamine	907	±
	Cyclopropylamine	900	−

[a] Reactions performed with a conventional FT-ICR instrument with addition of a noble gas to the ICR cell. The temperature of the system is not known, but assumed to be 300 K. [b] Values from ref. 3.

Results

The results for reactions of the immonium ions formed by α-cleavage [eqns. (1)–(3)] with various bases are collected in Table 1. These results were obtained with a conventional FT-ICR instrument (see the Experimental section) in which ion formation and the subsequent ion–molecule reactions occur in one and the same ICR cell. The reference base as well as the neutral precursor of the immonium ion will be present in the cell with the result that proton transfer to both compounds may occur as shown for $CH_2{=}NH_2^+$ in eqns. (4) and (5). Afterwards, the protonated reference base reacts with the precursor amine

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[†] The IUPAC recommended symbol for proton affinity (E_{pa}) is used in this paper. However, in many other publications proton affinity is abbreviated to PA.

Table 2 Thermochemical data obtained in this study

Imine	E_{pa}/kJ mol^{-1} [a]	ΔH_f^0/kJ mol^{-1}
CH_2=NH	854 ± 8	69 ± 8
CH_2=NMe	880 ± 4	44 ± 8
MeCH=NH	897 ± 5 [b]	24 ± 8
PhCH=NH	908 ± 7	

[a] See Table 1. [b] The E_{pa} obtained in ref. 12 for this compound was re-evaluated to be 895 kJ mol^{-1} on the basis of $E_{pa}(NH_3)$ = 853.5 kJ mol^{-1}. The E_{pa} was reproduced in this work with hexane-2,5-dione (E_{pa} = 892 kJ mol^{-1}) and allylamine (E_{pa} = 902 kJ mol^{-1}) as reference compounds.

[eqn. (6)]. The competing protonation of the amine and the

$$CH_2{=}NH_2^+ + B \longrightarrow CH_2{=}NH + BH^+ \tag{4}$$

$$CH_2{=}NH_2^+ + RCH_2NH_2 \longrightarrow CH_2{=}NH + RCH_2NH_3^+ \tag{5}$$

$$BH^+ + RCH_2NH_2 \longrightarrow B + RCH_2NH_3^+ \tag{6}$$

further reaction of BH^+ may obscure determination of reaction (4).

In order to test the reliability of the results in Table 1, we also studied reactions of the $CH_2{=}NH_2^+$ ion with a Bruker CMS 47X FT-ICR instrument equipped with an external ion source (see the Experimental section). The ions are here formed in the external electron impact (EI) ion source and transferred to the ICR cell where reactions with a substrate can occur without the disturbing influence of the neutral precursor of the ions. The $CH_2{=}NH_2^+$ ions formed externally and trapped in the ICR cell reacted readily with NH_3 and diethyl ether by proton transfer.

The ions may contain excess internal and/or translational energy, which can be used to induce an endothermic proton transfer. Neon was added, therefore, to the ICR cell through a pulsed valve until the pressure was *ca.* 10^{-3} Pa. At this pressure the ions undergo non-reactive collisions with the noble gas atoms, thus allowing for possible excess energy to be removed[21] before reaction with the reference base takes place. Under these conditions, proton transfer from $CH_2{=}NH_2^+$ to NH_3 or diethyl ether occurred only to a minor extent.

In the conventional FT-ICR instrument, thermalization of the immonium ions was ensured by addition of a noble gas to a pressure of *ca.* 10^{-4} Pa. Proton transfer from $CH_2{=}NH_2^+$ to NH_3 was barely observed and no reaction occurred with diethyl ether (Table 1). Without the addition of a noble gas to the ICR cell, $CH_2{=}NH_2^+$ transferred a proton to diethyl ether regardless of the competing reaction with the precursor amine. In combination, the results obtained with both FT-ICR instruments indicate that the thermochemical threshold for proton transfer can be derived from the occurrence of reaction (4) in the presence of the neutral precursor of the protonated imines if the ions are stabilized by collisions. The results in Table 1 have been used, therefore, to obtain the proton affinities of the imines. The values are given in Table 2.

Before discussing the proton affinities it should be mentioned that the ion formed in reaction (3) could have either of the two structures **1** or **2**.* It is known that the E_{pa} value of benzaldehyde is *ca.* 40 kJ mol^{-1} lower than the value for cyclohepta-2,4,6-trienone,[3] and a similar relative order can be anticipated for the proton affinities of the imines corresponding to the ions shown. With the experimental procedures used, the species with the lowest proton affinity is probed and the value in Table 2 is assigned to PhCH=NH.

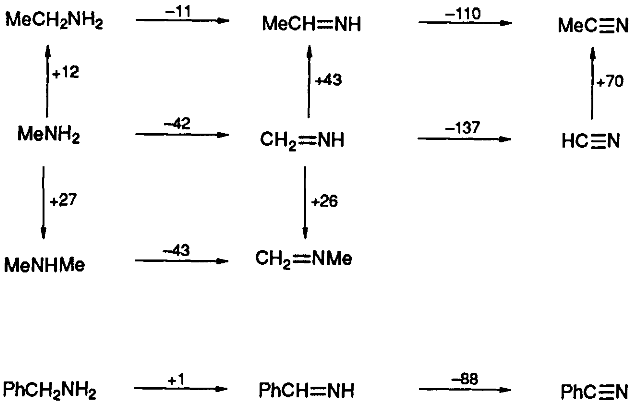
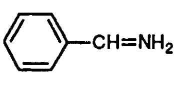


Fig. 1 Relative proton affinities of nitrogen-containing compounds as a function of the hybridization of the nitrogen atom and the introduction of a methyl or a phenyl group. The changes in the E_{pa} values are given in kJ mol^{-1}. [$E_{pa}(MeNH_2)$ = 896 kJ mol^{-1} and $E_{pa}(PhCH_2NH_2)$ = 907 kJ mol^{-1} (ref. 3).]



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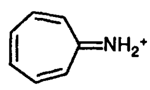

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Discussion

The proton affinities of the imines render it possible to assess the variation in intrinsic basicity of simple nitrogen-containing compounds in terms of hybridization, charge delocalization and methyl group effects. The differences in E_{pa} values of related amines, imines and nitriles are summarized in Fig. 1 for the purpose of discussion.

The experimentally determined decrease in E_{pa} on going from $MeNH_2$ to $CH_2{=}NH$ is 42 kJ mol^{-1}, while HCN is 137 kJ mol^{-1} less basic than the imine in the gas phase. A simple correlation between E_{pa} and the percentage s character of the nitrogen lone pair leads to the prediction that the difference in E_{pa} between the amine and the imine would be half of the difference between the imine and HCN. The observed difference in E_{pa} on going from the amine to the imine is smaller than expected from such a simple correlation, indicating that the relative loss in availability of the nitrogen lone pair for protonation in $CH_2{=}NH$ is partly compensated by delocalization of the charge in the protonated species.

The proton affinities of the other imines in Fig. 1 are also between the values of the corresponding amines and nitriles with the exception of the value for PhCH=NH, which is essentially the same as that of benzylamine. For this imine, delocalization of the charge into the phenyl group of the protonated species counterbalances the change in hybridization.

Alkyl groups are known to stabilize a negative as well as a positive charge owing to their polarizability.[22] This effect is dependent on the charge density on the atom bearing the alkyl group and on the distance of the charge with respect to the alkyl moiety; the latter effect is reflected for methyl as the alkyl group in the established order of E_{pa} for the amine series: $MeNH_2$ < $EtNH_2$ < MeNHMe. Introduction of a methyl group on the nitrogen atom in $CH_2{=}NH$ increases E_{pa} by 26

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* Preliminary collision-induced dissociation (CID) experiments performed with a ZAB-2HF double focussing mass spectrometer of reverse geometry gave no conclusive information about the extent to which the $C_7H_8N^+$ ions have the $PhCH{=}NH_2^+$ structure.

kJ mol^{-1}, whereas a more pronounced change is observed for methyl substitution at the carbon atom in line with calculations which reveal a large charge density at the latter position in the protonated imine.[9] Comparison of the effect of methyl/hydrogen substitution as a function of the hybridization of the nitrogen atom confirms the theoretical prediction that the charge density at the carbon atom is somewhat larger in protonated HCN than in the $CH_2{=}NH_2^+$ ion.[23,9]

The proton affinities of the imines can be used to obtain the heats of formation of these species since the ΔH_f^0 values of the immonium ions[24] are well known. The estimated values are given in Table 2. The ΔH_f^0 of $CH_2{=}NH$ is estimated, using eqn. (7) and $\Delta H_f^0(CH_2{=}NH_2^+)$ = 745 kJ mol^{-1}, to be 69 kJ mol^{-1}

$$\Delta H_f^0(CH_2{=}NH) = E_{pa} - \Delta H_f^0(H^+) + \Delta H_f^0(CH_2{=}NH_2^+) \quad (7)$$

and thus substantially lower than the previous experimentally obtained values of 111 and 105 kJ mol^{-1}.[25,26] The former value was based on the occurrence/non-occurrence of hydride ion transfer in reactions of $HCNH^+$ with alkanes or cycloalkanes.[25] Exothermic hydride ion transfer reactions can be slow in the gas phase[27] and for this reason may not be suitable for the determination of thermochemical parameters. The second value was derived from the kinetics of thermal decomposition of $\dot{C}H_2NH_2$ radicals into $CH_2{=}NH$, and it was reported that the value may represent an upper limit to the true value.[26] The present heat of formation of the imine is based upon a kinetic approach, but proton transfer reactions involving small ions are reported to occur at every collision with the substrate as long as the process is exothermic or thermoneutral.[28]

Upon the assumption that the ΔH_f^0 of the imine is as previously reported, we estimate that $CH_2{=}NH$ would have nearly the same E_{pa} value as $MeNH_2$, which is in contrast with the results obtained for the other imines studied. In conclusion, the heat of formation of $CH_2{=}NH$ derived in this work is likely to be closer to the true value than the earlier estimates.[25,26]

Experimental

The experiments were performed with a conventional home-made FT-ICR mass spectrometer and a Bruker CMS 47X instrument equipped with a 4.7 Tesla superconducting magnet and an external ion source.

Homemade FT-ICR.[29–32] The partial pressures of the amine and the reference base were *ca.* 2 × 10^{-5} Pa. The pressure in the ICR cell was increased up to 3 × 10^{-4} Pa by addition of helium or neon. The ions were formed by EI with 15 eV electrons and the immonium ions were isolated by notch ejection before they were allowed to react with the reference base. The occurrence of proton transfer from the immonium ions was confirmed by ion-ejection experiments. The inlet systems and the vacuum system were kept at room temperature.

Bruker CMS 47X.[33–35] The ions formed in the external ion source (temperature *ca.* 150 °C) by EI with 70 eV electrons were extracted from the source, focused into a beam and accelerated to a kinetic energy of 3 kV. Deceleration of the ions to low kinetic energies was achieved in the magnetic field and before the ions entered the cylindrical ICR cell kept at room temperature. The ions were trapped in the cell by applying a voltage of 1.0–1.5 V to the end plates of the cell. The ICR cell was filled with ions for 20–40 ms, after which the ion beam was deflected before reaching the deceleration region. The ions of interest were isolated by ejecting all other ions trapped in the ICR cell prior to reaction with the reference base (partial pressure 10^{-5} Pa). Addition of neon to the cell was achieved through a pulsed valve after the isolation of the immonium ions. The valve was open for 200 ms, and during this period the pressure increased up to 10^{-3} Pa.

Materials.—The compounds used were either commercially available or prepared by standard methods.

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