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Proton Transfer Chemistry in the Gas Phase. Is a Spontaneous 'Neutralization' Reaction a Myth or a Reality?*

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Abstract. Relying on physicochemical knowledge, the proton cannot be spontaneously transferred from a gaseous mineral acid (HF, HCl, HBr, HI, HNO_3, H_2SO_4, or $HClO_4$) to a gaseous nitrogen base (NH_3, alkylamine, aniline, pyridine, amidine, or guanidine). For example, the full proton-transfer from HCl to NH_3, followed by the separation of Cl^- and NH_4^+ requires more than 500 kJ mol^{-1}. The same is true for a spontaneous intramolecular proton-transfer for gaseous amino acids, aminophenols and other amphiprotic compounds. From the gas-phase acidity parameter of COOH and the gas-phase basicity parameter of NH_2 (or other more basic group in the side chain), it appears that proton transfer is endothermic or endergonic. For arginine, an amino acid with a highly basic guanidine function, this difference is still larger than about 300 kJ mol^{-1}. Only solvation of the acid-base system by neutral species (*e.g.*, one or more water molecules), complexation by ions (*e.g.*, ionic acids or bases, metal cations) or even electrons may reduce the energetic barrier and facilitate the proton-transfer. Recent extension of the gas-phase acidity-basicity scale toward superacids and superbases, and recent development of spectroscopic techniques adapted to the gas phase for less volatile organic compounds give some perspectives for observing the full intermolecular proton-transfer between a molecular Brønsted-Lowry superacid and a molecular Brønsted-Lowry superbase.

Keywords: acid-base chemistry, gas phase, acidity-basicity scale, proton-transfer, 'neutralization' reaction, superacids, superbases, amino acids, zwitterions

INTRODUCTION

First ideas on acid-base properties of chemical compounds and first definitions of acids and bases were born more than 300 years ago.[1–4] Proton-transfer reaction (1) for a conjugate acid-base pair was portrayed in 1923 by Brønsted[5,6] and independently by Lowry.[7,8] According to the Brønsted-Lowry definition, an acid (AH or BH^+), conjugated with a base (A^- or B), is a proton-donor, and a base is a proton-acceptor. Reactions (2) and (3) describe their contrasting properties. The quantitative Brønsted-Lowry definition contributes to various modern theories, which explain the structure, physicochemistry, chemical reactivity and biological activity of simple mineral and organic compounds, as well as more complex natural products, natural and synthetic drugs, toxicants, biopolymers, *etc.*[1–4,9–15]

$$\text{Acid} \rightleftarrows \text{Base} + \text{Proton} \qquad (1)$$

$$AH \rightleftarrows A^- + H^+ \qquad (2)$$

$$BH^+ \rightleftarrows B + H^+ \qquad (3)$$

Acid-base equilibria are well characterized in the gas phase and in solution.[1–4,9–11] A transfer of the proton from a molecular Brønsted-Lowry acid (AH) to a molecular Brønsted-Lowry base (B) is often called a 'neutralization' reaction in solution. However, there is no true point of neutrality. The name 'neutralization' has been historically taken from the Arrhenius theory,[1,2] according to which the molecular acid AH can react with the molecular base $M(OH)_n$ with the formation of the neutral water and electrically neutral salt molecules:

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* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.
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$$n\text{AH} + \text{M(OH)}_n \rightleftarrows \text{M}^{n+}(\text{A}^-)_n + n\text{H}_2\text{O}.$$

The Brønsted-Lowry proton-transfer between two neutral species, acid and base, and also within the same amphiprotic (*e.g.*, amino acids, peptides, proteins) or tautomeric (*e.g.*, nucleobases, nucleosides, nucleotides) molecule, is not accompanied by the formation of a neutral water molecule.[1–4,9–11] In solution, the proton-transfer reaction depends on acid-base strengths of reacting species, and also on solvating power of the solvent. The solvent molecules participate in this reaction. Interacting with the molecular and ionic species, they reduce the energetic gap for the proton transfer. In water or other polar solvents, the proton can be fully transferred according to reaction (4) if one or both partners are strong enough acid or base, and the ionic species can be formed. For weak acids and bases in less polar or non polar solvents, various types of complexes can be observed, from ion-pair (5), through proton-shared (6) to usual H-bonded complexes (7). Depending on solvent polarity, the reactants and products can be more or less solvated by solvent molecules.

$$\text{AH} + \text{B} \rightleftarrows \text{A}^- + \text{BH}^+ \tag{4}$$

$$\text{AH} + \text{B} \rightleftarrows [\text{A}^-\cdots\text{HB}^+] \tag{5}$$

$$\text{AH} + \text{B} \rightleftarrows [\text{A}^-\cdots\text{H}^+\cdots\text{B}] \tag{6}$$

$$\text{AH} + \text{B} \rightleftarrows [\text{AH}\cdots\text{B}] \tag{7}$$

The dilute gas phase can be considered as an ideal experimental medium in which the proton-transfer is free from solvation effects and depends solely on the acid-base strength of the reacting species. However, the deprotonation reactions for molecular (2) and ionic (3) acids are very endothermic (ΔH>>0) and very endergonic (ΔG>>0) in the gas phase. Their direct investigation is therefore difficult and requires more sophisticated methods and instruments than those applied for acid-base reactions in solution.

Kinetic and thermodynamic studies of proton transfer reactions in the gas phase started in the second half of the twentieth century, with the development of spectrometric techniques, *e.g.*, infrared (IR),[16] nuclear magnetic resonance (NMR),[17] microwave (MW),[18] and mass spectrometry (MS).[19–25] Indeed, the majority of the acidity and basicity parameters in the gas phase for mineral and organic compounds were determined using various MS techniques.[26–29] The greatest part of the gas-phase basicity data was critically evaluated in 1998 by Hunter and Lias.[30] All quantitative gas-phase proton-transfer determinations conducted for acids and bases have led progressively to a self-consistent gas-phase acidity-basicity scale.[26] This scale is qualitatively (ordering) and quantitatively (range) dissimilar to that found in aqueous solution.[1,2,9,31–34]

The aim of this review is to recall the principal thermochemical aspects of the proton-transfer reactions in the gas phase, in particular the investigations in the domain of spontaneous intra- and intermolecular proton-transfer from neutral acidic to neutral basic species. We also mention some of the reasons for which the spontaneous proton-transfer is exceptionally difficult to perform in the gas phase, in contrast to experiments that are relatively easily conducted in solution. It is also shown how proton transfer is facilitated in the gas phase by the presence of other species (like water molecules, ions, electrons).

ACIDITY-BASICITY SCALE IN THE GAS-PHASE

The enthalpy ($\Delta H°$) and the Gibbs (free) energy ($\Delta G° = \Delta H° - T\Delta S° = -RT\ln K$) of the deprotonation reaction for the molecular acid AH (2) and also for the ionic acid BH^+ (3) were proposed for the characterization of acidity and basicity in the gas phase.[9,23,26–34] When AH and BH^+ do not display a symmetry change nor a large structural change during the deprotonation reaction, the proton-transfer reaction is isentropic, *i.e.,* the entropy of this reaction is quasi-constant and close to the translational entropy of the proton, that is $T\Delta S° = 32.5$ kJ mol^{-1} at 298.15 K.[26–28,30] This aspect of the problem was discussed in our previous review paper on gas-phase proton transfer.[29]

Although the deprotonation of AH and BH^+ are similar processes, the corresponding thermodynamic parameters were traditionally given different symbols. For BH^+, conjugated with the neutral base B, the enthalpy and the Gibbs free energy of deprotonation are used as basicity parameters, and were called respectively proton affinity (PA) and gas-phase basicity (GB). For the neutral acid AH, the acidity parameters $\Delta H°$ and $\Delta G°$ were called $\Delta_{\text{acid}}H$ and $\Delta_{\text{acid}}G$. Here, these values are respectively referred to deprotonation enthalpy (DPE = $\Delta_{\text{acid}}H$) and gas-phase acidity (GA = $\Delta_{\text{acid}}G$). Both, the DPE and PA values are on the same enthalpy scale, and for a conjugated acid-base pair DPE(acid) = PA(base). Similarly, the GA and GB values are on the same Gibbs free energy scale, and for a conjugated acid-base pair GA(acid) = GB(base). A stronger acid has a smaller GA and DPE value in the acidity scale, and a stronger base has a larger GB and PA value in the basicity scale. Experimental and theoretical methods for determinations of acidity and basicity of chemical compounds in the gas phase were recently reviewed.[29,34]

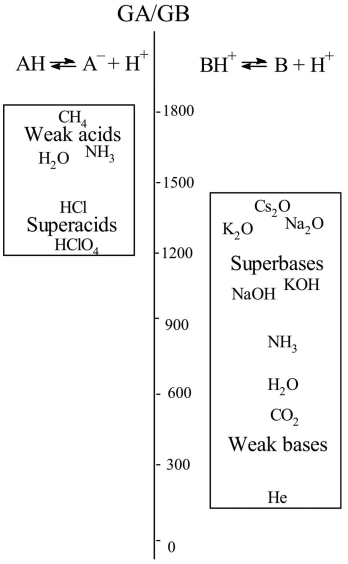


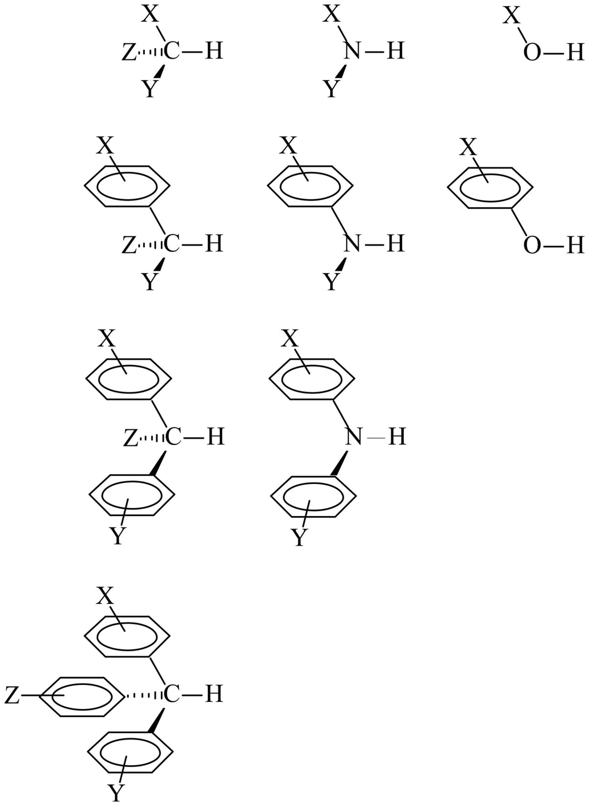
Figure 1. Generalized gas-phase acidity-basicity scale (GA/GB expressed in kJ mol^{-1} at 298 K).

Figure 1 illustrates the generalized acidity/basicity scale (GA/GB scale) constructed on the basis of experimental data reported in the literature for the gas phase.[26,30,35–38] The molecular acids include the families of CH, NH, OH, PH, SH, and other simple protogenic acids XH. Their GA values are between 1200 and 1800 kJ mol^{-1} (remember that higher values correspond to weaker acids). Many molecular organic CH, NH and OH acids are stronger in the gas phase than mineral acids such as HF, H_2S, HCN, HCl, HNO_3, HBr, HI, and H_2SO_4. Perchloric acid ($HClO_4$) is probably the strongest acid in the current acidity scale, but its GA value is known with a large uncertainty of about 60 kJ mol^{-1}.[39] The neutral bases include the families of noble gases, atomic or molecular elements, oxides, hydroxides, and other bases containing nitrogen, oxygen, sulfur, or π-electron systems. Their GB values are between 150 and 1450 kJ mol^{-1} (remember that higher values correspond to stronger bases). Alkali metal oxides (Na_2O, K_2O, and Cs_2O) have the largest PA and GB values in the current basicity scale.[26,30,36–38] Among organic compounds, nitrogen bases with the amidine, guanidine and phosphazene functions have the GB values close to those for alkali metal hydroxides (NaOH, KOH, and CsOH). The GB values of some substituted phosphazenes, vinamidines and Verkade's bases are even larger than that of CsOH.[36,37]

The gas-phase acidity and basicity scales overlap only for the strongest acids and bases because the deprotonation reaction of AH (2) requires in general a greater energy than that of BH$^+$ (3).[9,23,26–34]Therefore, the GA/GB scale, established for the gas phase, is fundamentally different from that for aqueous solution.[9,26–34] The principal difference between the scales results mainly from solvation energies which are more than 10 times larger in water for the ionic than molecular forms.[40] Any solvation of the ionic and molecular forms changes dramatically the relative acidity/basicity determined in the dilute gas. Consequently, the acidity and basicity scales in aqueous solution cover almost the same range of pK_a values.[1,34]

GAS-PHASE SUPERACIDS

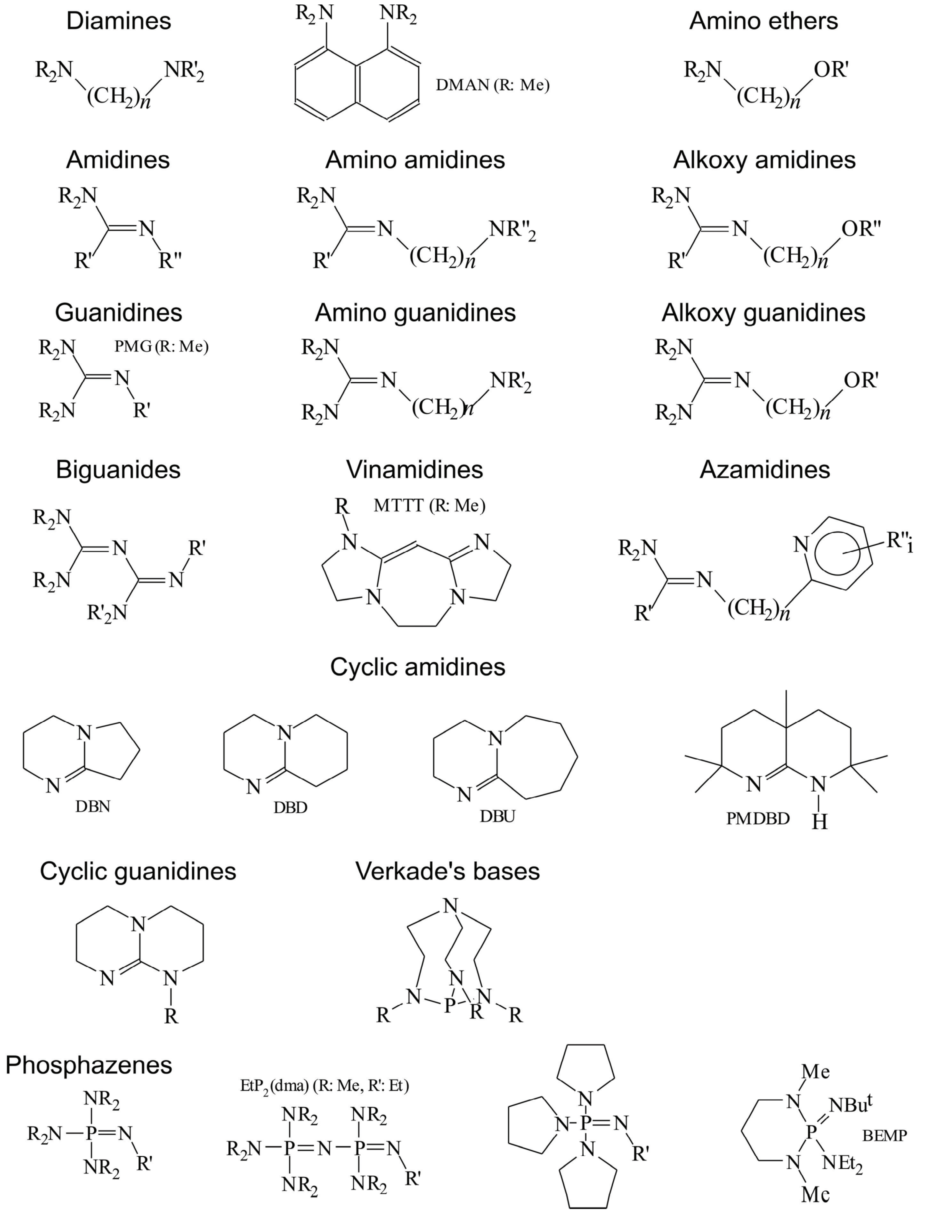
Systematic experimental investigations on strong organic acids in the gas phase were carried out at the University of California, Irvine (USA) in the laboratory of R. W. Taft (deceased in 1996) in collaboration with I. A. Koppel at the University of Tartu (Estonia).[35] Acids stronger than H_2SO_4 (GA<1255 kJ mol^{-1}) were defined as gas-phase superacids, similarly as superacids defined in solution (stronger than 100 per cent H_2SO_4).[4,41–43] Gas-phase superacids include the families of CH, NH, OH organic acids (Scheme 1) which contain strong, or very strong, electron-accepting group(s) X, Y and/or Z, such as CF_3, COR, C_6F_5, 4-C_5F_4N, $C(CF_3)_3$, CN, NO_2, SO_2R, COCN, C=NSO_2CF_3, SO(=NSO_2CF_3)CF_3, and S(=NSO_2CF_3)$_2CF_3$. These groups may be directly linked to the C, N, or O atom, or separated by a phenyl ring.



Scheme 1. Families of selected CH, NH and OH organic acids.

Among organic acids, XOH are, generally, stronger than XNH_2 and XCH_3.[26,35] For example, the GA value for CF_3COOH (1328 kJ mol^{-1}) is lower (stronger acid) than that of CF_3CONH_2 (1409 kJ mol^{-1}) and CF_3COCH_3 (1431 kJ mol^{-1}). Similarly, the GA value for CF_3SO_2OH (1253 kJ mol^{-1}) is lower than that of $CF_3SO_2NH_2$ (1344 kJ mol^{-1}) and $CF_3SO_2CH_3$ (1422 kJ mol^{-1}). Analysis of substituent electronic effects performed for strong organic acids[35] showed strong domination of the resonance (R) effect for the CH acids. Its contribution to the total electronic effect slightly decreases for the NH acids in favor of the field/inductive (F) and polarizability (P) effects. For the OH acids, all effects (R, F and P) are very important and influence the GA values.

Multiple substitution of methane and ammonia by strong electron-accepting groups leads to very strong organic acids.[35] Although the substituent effects are not additive for multiply substituted CH and NH acids, many X_3CH acids are stronger than X_2NH and XOH acids. For example, the GA value for $(CF_3CO)_3CH$ (1258 kJ mol^{-1}) is lower than that of $(CF_3CO)_2NH$ (1287 kJ mol^{-1}) and CF_3COOH (1328 kJ mol^{-1}). Similarly, the GA value for $(CF_3SO_2)_3CH$ (1209 kJ mol^{-1}) is lower than that of $(CF_3SO_2)_2NH$ (1221 kJ mol^{-1}) and CF_3SO_2OH (1253 kJ mol^{-1}). Currently, $(C_4F_9SO_2)_2NH$ (GA 1189 kJ mol^{-1}) is the most acidic in the experimental gas-phase superacidity scale for organic compounds.[35] Noteworthy, the fluorinated compounds are generally volatile enough to be studied by most of the



Scheme 2. Families of selected organic bases.

mass spectrometry techniques. The strongest acid in this scale is probably the mineral acid $HClO_4$ (GA 1180±59 kJ mol^{-1}).[39]

GAS-PHASE SUPERBASES

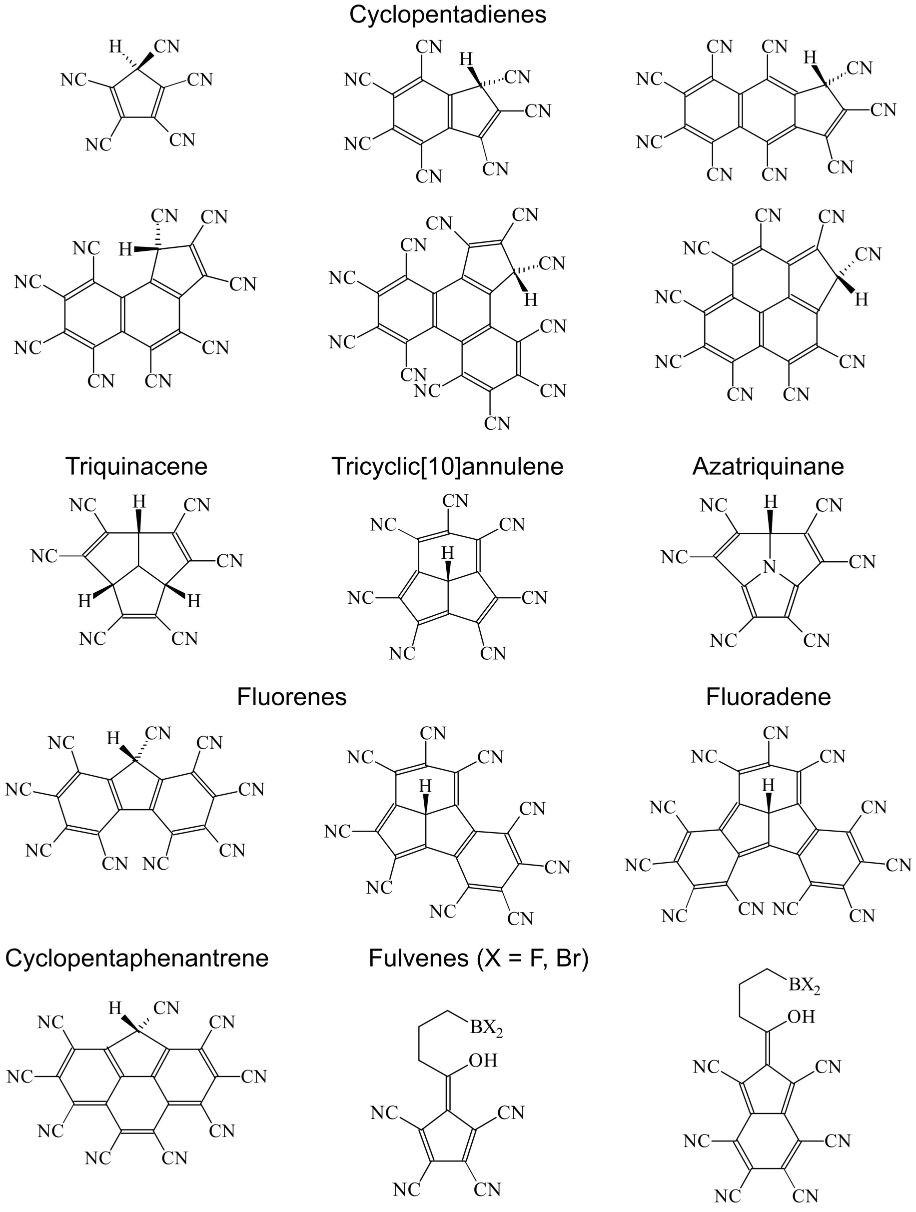
Superbases in the current experimental gas-phase basicity scale (Figure 1) include the families of organic bases (Scheme 2): diamines, amidines, guanidines, biguanides, vinamidines, phosphazenes and Verkade's bases.[26,30,36–38] They include also the families of inorganic bases: hydroxides (MOH, M = Li, Na, K, Cs), oxides (M_nO, $n = 1$: M = Ca, Sr, Ba; $n = 2$ Li, Na, K, Cs), hydrides (MH, M = Li, Na) and even mono- or diatomic species (La, Na_2, L_2).[26,30] The strong gas-phase basicity (large GB) of α,β-, α,γ-, ..., and α,ω-alkyldiamines was experimentally observed about thirty years ago independently by D. H. Aue, M. T. Bowers, P. Kebarle, M. Meot-Ner (Mautner) and their co-workers.[23,44–47] The first systematic investigations on the gas-phase basicity of amidines were carried out about twenty years ago by one of us in collaboration with R. Houriet at the Ecole Polytechnique Fédérale de Lausanne (Switzerland).[48] Subsequently, they were continued at the Université de Nice - Sophia Antipolis (France).[36,49–56] These measurements opened the possibilities to study the gas-phase basicities of very strong organic bases: cyclic or acyclic amidines and guanidines, amino amidines (including histamine and its *N*,*N*-dimethyl derivative), amino guanidines (including arginine), biguanides, vinamidines and phosphazenes, some of them being used, and commercialized, for their catalytic properties. Investigations on substituted phosphazenes and Verkade's bases, the strongest bases in the current gas-phase basicity scale, were undertaken a few years ago by I. A. Koppel and his group, and the gas-phase measurements performed in collaboration with the M. Mishima group at the Kyushu University, Fukuoka (Japan).[37,57] For some guanidines with heteroalkyl side chains, measurements were also carried out by Z. Glasovac *et al.*[38] in the H. Schwarz laboratory, Technical University of Berlin (Germany). For the most basic α-amino acid arginine containing the guanidine group at the end of the side chain, the gas-phase basicity was firstly reported by Z. Wu and C. Fenselau,[58] and recently reexamined by Bouchoux *et al.*[59] The gas-phase basicity for histamine was determined by us[51] and independently for histamine and its *N*,*N*-dimethyl derivative by J.-L. M. Abboud and his co-workers.[60,61]

Strong organic nitrogen bases contain aryl, heteroaryl, simple alkyl, arylalkyl, and heteroalkyl groups.[23,26,30,36–38,44–61] The aryl, alkyl and arylalkyl groups increase the gas-phase basicity (increase GB) mainly by their strong polarizability effect. This effect is reduced almost to zero in aqueous solution.[31–33] The heteroalkyl and heretoaryl groups containing basic groups (*e.g.*, OMe, NMe_2, 2-pyridyl) at the end of the chain may additionally chelate the proton and augment the GB values by formation of intramolecular ionic H-bonds ($X\cdots H{-}B^+$), similar to those for diamines, amino ethers, diethers.[45–47,62,63] This effect, called 'internal solvation',[45–47] is able to increase the GB values of superbases by 20−100 kJ mol^{-1}.[36,38,50–52,54,56] Derivatives containing the $(CH_2)_3NMe_2$ group are the strongest bases in the families of amines, amidines and guanidines. It is possible that this alkylamino group induces also an increase toward the strongest basicities encountered in the family of phosphazenes. In aqueous solution, the 'internal solvation' effect is only maintained for bidentate nitrogen ligands with a rigid conformation (proton sponges, *e.g.*, DMAN, Scheme 2).[64] In the case of ligands with a flexible conformation, the external solvation by water molecules is stronger than the 'internal solvation', and destroys the $X\cdots H{-}B^+$ bridges. This brings typical basicities in aqueous solution for bidentate ligands with a flexible conformation close to those for monobases.[65]

Generally, experimental gas-phase basicity of nitrogen bases containing similar R and R' groups increases in the following order: $RNR'_2 < RN{=}CHNR'_2 < RN{=}C(NR'_2)_2 < RN{=}P(NR'_2)_3 < RN{=}P(NR'_2)_2{-}N{=}P(NR'_2)_3$. The same is true for the cyclic systems: amines < amidines < guanidines < phosphazenes, vinamidines, Verkade's bases. Amidines, guanidines, phophazenes, biguanides and vinamidines are stronger bases than the corresponding amines and imines due to strong 'push-pull' effect between the electron-donor (NR'_2) and electron-acceptor group (C=N or P=N). The 'push-pull' effect stabilizes strongly the monoprotonated cations. This phenomenon has been discussed in our previous papers on superbases in the gas phase.[36,54] Currently, phophazene $EtN{=}P(NMe_2)_2{-}N{=}P(NMe_2)_3$ (GB 1107 kJ mol^{-1}) is the strongest organic base in the experimental superbasicity scale.[37]

THEORETICAL PROPOSALS FOR SUPERACIDS AND SUPERBASES

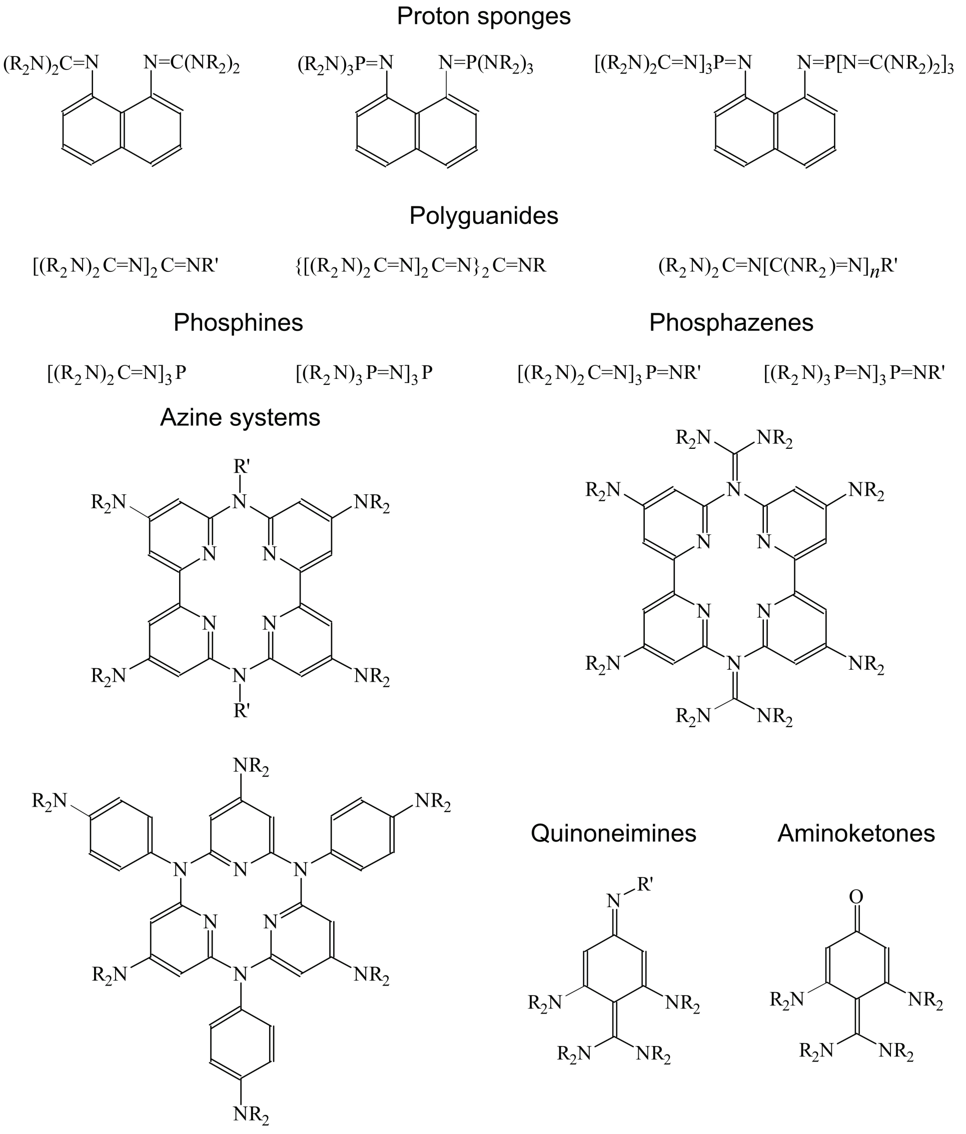
The CH, NH and OH acids containing the Yagupolski superacceptors as substituent(s),[66,67] obtained by replacing the X=O (X = C, S, N, …) group by $X{=}NSO_2CF_3$, were proposed as prospective candidates for extending the gas-phase superacidity scale.[68] Mineral acids (HNO_3, H_2SO_4 and $HClO_4$) similarly modified along the Yagupolski concept seem to be also very good candidates as superacids.[68] Moreover, strong acidity was theoretically



Scheme 3. Selected candidates for superacids in the gas phase.

proved for polysubstituted carboranes, cyclopentadienes, fluoradenes, fulvenes, fluorenes, azatriquinanes and other polysubstituted planar hydrocarbons containing electron-accepting groups (*e.g.*, CF_3, CN or SO_2CF_3).[68–81] The acidities, estimated for most of them, are in the range 1000−1300 kJ mol^{-1}. Some examples of polycyano derivatives − candidates for superacids − are given in Scheme 3. Among other candidates as superacids, carboranes attracted recently special attention of chemists.[82–87] The carborane anion $CB_{11}H_{12}^-$ has been recognized as potential building block for the ultimate superacid. Its modifications by substituting hydrogens by halogens (F, Cl, Br, and I), methyl or fluorinated groups (like trifluoromethyl) lead to the family of compounds which may protonate weakly basic molecules such as alkenes, benzene, and even the Xe atom.

Solely for few derivatives from the families of vinamidines, polyguanides, phophazenes, and Verkade's bases, the gas-phase basicity could be measured. Due to experimental difficulties, principally the lack of reference compounds, most potential superbases such as substituted phosphazenes, guanidino phosphazenes, guanidino and phosphazeno derivatives of diamines, polyguanides, and Verkade's bases were investigated theoretically.[88–95] Quinoneimines, [3]iminoradialenes, cyclopropeneimines, 2,5-dihydropyrrolimines, iminopolyenes, conjugated iminoamines, quinones, [3]carbonylradialenes, azine systems, and sulfilimines were also



Scheme 4. Selected candidates for superbases in the gas phase.

proposed as further possible classes of superbases.[96–109] The basicities calculated for most of them are in the range 1000−1400 kJ mol^{-1}. Some examples of candidates for superbases are given in Scheme 4.

All theoretical investigations for strong acids and strong bases substantiate the observed experimentally gas-phase internal effects, such as enhancement of both acidity and basicity by the high polarizability effect of alkyl and aryl groups, acidity strengthening by the strong electron-accepting inductive/field effect of CF_3, CN, NO_2 and SO_2CF_3 group, and basicity strengthening by the push-pull effect for conjugated amino-imino, amino-phosphoimino, and amino-sulfoimino systems, and by the 'internal' solvation for polydentate ligands. The acidities and basicities computed for very strong acids and very strong bases expand the GA/GB overlap between organic superbases and organic superacids in the current experimental acidity-basicity scale (Figure 2).

It should be mentioned here that in order to obtain acidity/basicity parameters to 'benchmark' accuracy (1 kJ mol^{-1}), very high levels of correlation, *e.g.*, CCSD(T) (coupled-cluster method including all single and double excitations with perturbative terms for triple excitations) or QCISD(T) (quadratic configuration interaction withsingle and double excitations including triple excitations), and very large basis sets, *e.g.*, 6-311+(3df,2p) or aug-cc-pVTZ (augmented correlation consistent polarized valence triple zeta), have been recommended.[110,111] Among other quantum-chemical methods proposed to obtain data to 'chemical' accuracy (5 kJ mol^{-1}), *i.e.*, an accuracy equivalent to (or even better than) that of most experimental values, the Gaussian-2 (G2) theory is the most popular.[112,113] The G2 energy corresponds effec-

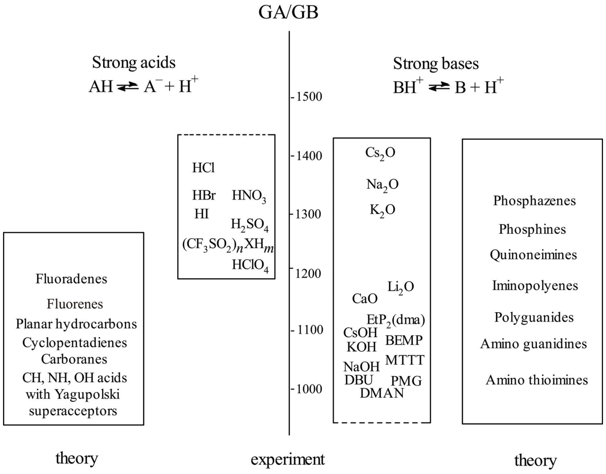


Figure 2. Overlap in experimental and theoretical gas-phase acidity and basicity scales in the region of strong acids and strong bases (GA/GB in kJ mol^{-1} at 298 K). (Acronyms and structures: see schemes)

tively to a QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31(d) energy with zero-point vibrational and empirical 'higher-level' corrections (MP2 – 2nd order Möller Plesset perturbation). Most density functional theory (DFT) methods are able to produce GA/GB (or DPE/PA) data within about 10–20 kJ mol^{-1} of experimental results.[114–116] Theoretical proposals for superacids and superbases were mainly based on restricted Hartree-Fock (HF), MP2, G2, and DFT calculations with a hybrid exchange-correlation functional, B3LYP.[66–109]

'NEUTRALIZATION' REACTION IN THE GAS PHASE

According to the Brønsted-Lowry theory, the acid-base reaction refers to the intermolecular proton-transfer from an acid to a base (ionic or molecular, strong or weak). The proton-transfer between molecular species (4) is a 'neutralization' reaction. The 'neutralization' reaction and also the proton-transfer between a molecular acid and an ionic base (8) or a molecular base and an ionic acid (9) are typical reactions between two conjugate acid-base pairs. All of them can be described by one general acid-base equilibrium (10). The Gibbs (free) energy ($\delta_{PT}\Delta G°$) of this reaction refers to the difference between acidity (or basicity) parameters (11), *i.e.*, to the difference between acidity of AH and BH$^+$ (equal to the relative basicity of A$^-$ and B) for reaction (4), to the difference between acidity of A$_1$H and A$_2$H (equal to the relative basicity of A$_1^-$ and A$_2^-$) for reaction (8), and to the difference between acidity of B$_1$H$^+$ and B$_2$H (equal to the relative basicity of B$_1$ and B$_2$) for reaction (9). The proton may be spontaneously transferred when $\delta_{PT}\Delta G°$ has a negative value and if there is no transition state between the reactants and products with an energy higher than that of the initial reactants.

$$A_1H + A_2^- \rightleftarrows A_1^- + A_2H \qquad (8)$$

$$B_1H^+ + B_2 \rightleftarrows B_1 + B_2H^+ \qquad (9)$$

$$\mathrm{Acid}(1) + \mathrm{Base}(2) \rightleftarrows \mathrm{Base}(1) + \mathrm{Acid}(2) \qquad (10)$$

$$\begin{aligned} &\delta_{PT}\Delta G° = \mathrm{GA}\big[\mathrm{Acid}(1)\big] - \mathrm{GA}\big[\mathrm{Acid}(2)\big] \\ \text{or}\quad &\delta_{PT}\Delta G° = \mathrm{GB}\big[\mathrm{Base}(1)\big] - \mathrm{GB}\big[\mathrm{Base}(2)\big] \end{aligned} \qquad (11)$$

Most of the current MS determinations of the gas-phase acidity-basicity strength are based on the concept of the proton-transfer reactions (8) and (9) between molecular and ionic species.[9,26–37] The relative acidities or basicities could be measured if the differences are not larger than about 10 kJ mol^{-1}. However, only considering the experimental GA and GB of Figure 2, the full transfer of the proton (4) from a typical molecular Brønsted-Lowry acid to a typical molecular Brønsted-Lowry base requires much more (Gibbs) energy in the gas phase (Table I), and thus is not yet achievable using MS techniques.[54,117–121] For example, the endothermic (endergonic) proton transfer from the mineral acid HI and the carboxylic acid CF_3COOH to amines has been observed in crossed beam experiments in which the kinetic energy of reactants supplies the lacking amount of energy.[117,118] Other spectroscopic techniques such as IR, MW, NMR were applied only for simple acids (*e.g.*, HF, HCl, HBr, HI, HNO_3) and bases (*e.g.*, NH_3, amines, pyridines).[16–18,122–143] Depending on the strength of the acid and the base, various interactions were observed between molecular acidic and basic species, from H-bonded ion-pairs (5) through proton-shared H-bonds (6) to usual H-bonds (7). In the case of IR techniques, these interactions depend also on the type of matrix applied. For complexes of amines with hydrogen halides, the extent of proton transfer was observed to increase for more polarizable matrix (*e.g.*, from Ar to the more polarizable N_2 matrix). In N_2 matrix, the proton is almost completely transferred from hydrogen bromide to the nitrogen atom of trimethylamine whereas it is still shared between the nitrogen and bromine atoms for complexes with ammonia.[134] However, in the case of pyridine complexes with the less acidic hydrogen chloride, the proton is not transferred from chlorine to nitrogen atom for any dimers in Ar as well as in N_2 matrix.[142] This observation is in agreement with the acidity/basicity scale and with an increased stabilization of H-bonded ion pairs (5) by the polarizable matrix, analog to a 'solvent' polarizability effect, and which is also

Table 1. Gibbs (free) energies ($\delta_{PT}\Delta G°$ / kJ mol^{-1} at 298 K)[(a)] required for the full intermolecular proton-transfer (4) in the gas phase between the molecular acid AH and the molecular base B with separation of the ions

	$\delta_{PT}\Delta G°$						
B/AH	HF	HCl	HBr	HNO_3	HI	H_2SO_4	$HClO_4$
NH_3	710	554	513	511	475	432	361
Aniline	679	522	481	479	443	400	329
Pyridine	631	475	434	432	396	353	282
Me_3N	611	455	414	412	376	333	262
Acetamidine	591	435	394	392	356	313	242
Guanidine	580	423	382	380	344	302	231
DMAN	534	377	336	334	298	255	184
DBU	514	357	316	314	278	236	165
BEMP [(b)]	458	302	261	259	223	180	109
Et-P_2(dma) [(b),(c)]	422	266	225	223	187	144	73

[(a)] Estimated according to relation (11). Gas-phase acidity and basicity parameters for AH and B were taken from Ref. 26.

[(b)] Basicity parameters taken from Ref. 37.

[(c)] Et-P_2(dma): $EtN{=}P(NMe_2)_2{-}N{=}P(NMe_2)_3$.

Table 2. Gibbs (free) energies ($\delta_{PT}\Delta G°$ / kJ mol^{-1} at 298 K)[(a)] required for the full intramolecular proton-transfer in the gas phase between COOH and NH_2 (or more basic group in the side chain) of α-amino acids

α-Amino acid	$\delta_{PT}\Delta G°$	α-Amino acid	$\delta_{PT}\Delta G°$
Glycine	553	Tryptophan	477
Alanine	533	Methionine	476
Valine	525	Threonine	470
Proline	516	Aspargine	464
Isoleucine	510	Glutamine	456
Leucine	509	Aspartic acid	441
Phenylalanine	500	Glutamic acid	440
Cysteine	497	Lysine	436
Tyrosine	492	Histidine	396
Serine	481	Arginine	345

[(a)] Estimated according to relation (11). Gas-phase acidity and basicity parameters for α-amino acids were taken from Refs. 26 and 149.

reflected in the gas phase basicity parameter for noble and molecular gases (He < Ne < Ar < Kr < N_2 < Xe).[26,30] Therefore, the results obtained in IR matrix experiments exhibit a significant environmental effect and thus they cannot be put in the same class as those in the dilute gas phase.

Particular cases are α-amino acids, which possess the acidic and basic groups within the same molecule. They belong to the family of bi- (or poly-) functional compounds displaying amphiprotic properties. The proton may be intramolecularly transferred from the acidic to basic group, and α-amino acids may exist as the unionized [$H_2NCH(R)COOH$] and/or zwitterionic forms [$^+H_3NCH(R)COO^-$ or $H_2NCH(RH^+)COO^-$, for nonbasic and basic amino acids, respectively]. Considering the acidity parameters of the carboxylic groups and the basicity parameters of the basic functions in α-amino acids, they should exist in the unionized forms in the gas phase.[144] Although it was speculated that the zwitterionic form of the most basic arginine may exist in the gas phase,[145] the spontaneous intramolecular proton-transfer from the carboxyl to guanidine group is not energetically possible (Table II). The reaction is very endergonic. Difference between the acidity-basicity parameters of the acidic and basic groups is very high ($\delta_{PT}\Delta G°$>300 kJ mol^{-1}).[26,30,58,59,146–149] The absence of zwitterionic forms for isolated α-amino acids was confirmed by various spectroscopic techniques such as electron diffraction, IR matrix isolation or cavity ringdown, microwave and MS.[145,150–155]

IMPORTANCE OF ENVIRONMENT ON PROTON-TRANSFER

Microsolvation of acid-base system in the gas phase by one or more molecules (water or other acidic or basic species), by interaction with metal cations or other ions, and by electron(s) may alter the thermochemistry of the isolated system (*i.e.*, reduce the difference between acidity and basicity parameters) and prompt the proton-transfer reaction. It may be noticed that photon(s) may lead to proton transfer, by simply bringing energy to the system. One can find numerous examples in the literature that substantiate these environmental effects. In this paper, we discuss a few of them.

The change of the acidity-basicity parameters when proceeding from the isolated molecules ($\delta_{PT}\Delta G$) to the micro- or macrosolvated [$\delta_{PT}\Delta G(\text{sln})$] acid-base system (Scheme 5) results entirely from differences in solvation energies ($\Delta_{sol}G$, always negative) between neutral and ionic forms, as shown in relation (12).[31–34,40,156] Note that (sln) refers to the physical state (solution), and that (sol) refers to the process of solubilization. The solvatation energies for neutral acids (AH) and bases (B) in water are about one order of magnitude lower than those for anionic bases (A^-) and cationic acids (BH^+). Therefore, ion solvation is an essential aspect of the change of the acidity-basicity parameters when going from the gas phase to strongly solvating media.

The great differences between the solvation energies for the neutral and ionic forms explain, for example, why NH_3 is protonated by HCl in water [reaction is exergonic, $\delta_{PT}\Delta G(\text{sln}) = -59$ kJ mol^{-1}],[65] whereas in the gas phase the H-bond between neutral species ($H_3N\cdots HCl$)[122,123] formed [reaction (4) is highly endergonic, $\delta_{PT}\Delta G = 554$ kJ mol^{-1}].[26] The nature of the H-bond complex has been also examined by matrix isolation studies.[130] To observe the proton-transfer in the gas phase, the $NH_3\cdots HCl$ complex has to be microsolvated by species capable to reduce the energy gap. According to theoretical considerations, the first added water molecules seem to play a critical role in assisting proton transfer in $NH_3\cdots HCl$. Tao and co-workers[157] found at the MP2/6-311++G(d,p) level of theory that the first water molecule induces a nearly flat potential energy pathway for proton transfer, but at least two water molecules must to be involved for the complete proton transfer from HCl to NH_3. They reported similar results for interactions and proton transfer reactions of halosulfonic (HSO_3X, X = F, Cl, Br) and methanesulfonic acids ($MeSO_3H$) with NH_3.[158,159] Latajka and Biczysko[160] confirmed the finding for the $NH_3{-}HCl{-}(H_2O)_2$ complex (tetramer) by calculations at the B3LYP/6-311++G(d,p) level. However, using the same method and a larger basis function (aug-cc-pVDZ), Li *et al.*[161] concluded that one water molecule is sufficient for the proton transfer occurring from HCl to NH_3 in their complex. Asada *et al.*[162] confirmed also that the theoretical structure of hydrated $NH_3{-}HCl$ clusters strongly depends on the basis set applied in calculations. At the MP2/aug-cc-pVDZ level, the most stable trimer $NH_3{-}HCl{-}H_2O$ has a proton-transfer structure. However, independently to the level of calculations, all these theoretical results show clearly that the water molecule(s) may change the character of the $NH_3{-}HCl$ complex from a simple adduct ($H_3N\cdots HCl$) to an ion pair complex ($H_3N^+H\cdots Cl^-$). They also explain why during the interdiffusion experiment with the vapors from aqueous HCl and NH_3 solutions the ionic ammonium chloride particles were produced.[163] In this kind of experiment, water vapor was unavoidable.[157] On the contrary, in the microwave experiments of Legon and co-workers[122,123] with the vapor from dry ammonium chloride crystals, the system observed is a simple H-bonded complex with HCl as the H-bond donor and NH_3 as the H-bond acceptor.

$$
\begin{aligned}
\delta_{PT}\Delta G(\text{sln}) = \delta_{PT}\Delta G - \Delta_{sol}G(AH) - \Delta_{sol}G(B) + \\
\Delta_{sol}G(A^-) + \Delta_{sol}G(BH^+)
\end{aligned}
\qquad (12)
$$

$$\begin{tikzcd}
\text{isolated} & AH \arrow[d, "\Delta_{sol}G(AH)"] & + & B \arrow[d, "\Delta_{sol}G(B)"] \arrow[r, shift left, "\delta_{PT}\Delta G"] & A^- \arrow[l, shift left] \arrow[d, "\Delta_{sol}G(A^-)"] & + & BH^+ \arrow[d, "\Delta_{sol}G(BH^+)"] \\
\text{solvated} & AH_{sol} & + & B_{sol} \arrow[r, shift left, "\delta_{PT}\Delta G(\text{sln})"] & A^-_{sol} \arrow[l, shift left] & + & BH^+_{sol}
\end{tikzcd}$$

Scheme 5. Thermodynamic cycle for 'neutralization' reaction when going from isolated to solvated system.

Besides water molecules, proton transfer may also be promoted in the $NH_3{-}HCl$ complex by the presence of other molecules. For example, Li and co-workers[164] investigated by computations [MP2/6-311++G(2d,2p)] the systems microsolvated by only one molecule. They considered various acidic, neutral and basic species (AH) and concluded that a molecule AH plays the role of a catalyst for the proton transfer within the cyclic trimer (Chart 1), when the sum of the two H-bonds

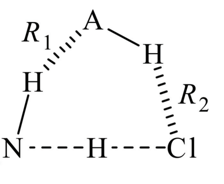


Chart 1.

lengths (R_1 and R_2) is shorter than 5.0 Å. This was found for AH = H_2SO_4, H_2SO_3, HCOOH, HF, H_2O_2, HNO_3, HNO_2, CH_3OH, HCl, HNC, H_2O, HCHO. The proton transfer was not observed for AH = HCN, H_2S and PH_3.

Recently, Eustis *et al.*[165] investigated the effect of an excess electron by anion photoelectron spectroscopy and also by *ab initio* calculations, and suggested that electron solvation induces the $NH_3{\cdots}HCl$ complex to form the ionic salt $NH_4^+Cl^-$. It is evident that the two complexes, $NH_3{\cdots}HCl$ and $NH_4^+Cl^-$, are no longer neutral after addition of an electron, but it may be considered that we are dealing with a limiting case of the effect of an electric field on proton transfer within a neutral system. An experiment with the vapor from dry ammonium chloride crystals should be performed for comparison.

α-Amino acids are derivatives for which the proton may be intramolecularly transferred from the acidic to the basic group. This transfer was extensively studied by both experimental and theoretical methods. It is well known that macrosolvation of α-amino acids by the solvent water leads to the zwitterionic forms for all derivatives. The proton is completely transferred, because the difference between the aqueous acidity of the acidic group and the aqueous basicity of the basic group is energetically profitable. Reaction is exergonic [$\delta_{PT}G(\text{sln}) < -25$ kJ mol^{-1}].[1,166] For arginine and lysine, the guanidine and amine function, respectively, present in the R group, are more basic in aqueous solution than the NH_2 function at the $^{\alpha}$C atom, and thus they may preferentially attach the proton from the COOH group. The water molecules participate in the intramolecular proton-transfer and stabilize the positive and negative charges in the zwitterionic structures.

How many solvent molecules would stabilize the zwitterionic form is a fundamental question concerning the zwitterion solvation. Although there are numerous theoretical and experimental works in the literature which try to answer this question, no common conclusions and no common theories which could explain the stepwise solvation process from the 'canonical' (isolated) molecule to the fully solvated zwitterionic structure exist. It has been shown by quantum-chemical calculations performed for isolated amino acids that one water molecule seems to be insufficient to stabilize the glycine (Gly), alanine (Ala), serine (Ser), phenylalanine (Phe), tryptophan (Trp), and other amino acid zwitterions.[167–178] For example, two water molecules may stabilize the Gly-zwitterion in a local minimum.[167] Petenau and Levy found by resonance-enhanced two-photon ionization (UV spectroscopic) experiments carried out for singly hydrated neutral Trp that the amine group is the favored site of water binding.[179] Using doubly resonant two-photon ionization (R2PI), UV hole burning (specific excitation and depletion of a specific species), IR-dip (dip in the ion signal due to irradiation at a specific vibrational mode), and MS experiments, Simons and co-workers[180–182] suggested that the Trp molecule solvated by up to three water molecules forms the zwitterionic structure. The gradual transition to the Trp-zwitterion with increasing cluster size of water (from one to six molecules) and methanol (from one to nine molecules) was recently reported by Blom *et al.*[183] who applied IR-dip spectroscopy to study the spectral signatures for the $-NH_3^+$ and $-COO^-$ groups ($-COO^-$ stretch and $-NH_3^+$ bending modes) of $\text{Trp}(H_2O)_n$ and $\text{Trp}(\text{MeOH})_n$. Taking these experiments into account, they concluded that the transition from canonical to zwitterionic structures appears to be gradual and competitive in energy for the highest number of water molecules studied, $\text{Trp}(H_2O)_6$. For the $\text{Trp}(\text{MeOH})_n$ complexes evidence was found that a minimum of five solvent molecules are necessary to observe a zwitterionic structure. Among other amino acids possessing aromatic UV chromophores, the hydrated complexes of phenylalanine (Phe) were investigated by R2PI and *ab initio* calculations, and it was suggested that the water molecule forms a cyclic H-bond at the COO^- group.[184]

The dipole-bound electron may also stabilize the amino acid zwitterion.[185–189] Bowen and co-workers[190] investigating the 'solvation number' onset for the formation of $\text{Gly}{\cdot}e^-(H_2O)_n$, $\text{Phe}{\cdot}e^-(H_2O)_n$, and $\text{Trp}{\cdot}e^-(H_2O)_n$ suggested that a minimum of five water molecules are needed to transform the Gly anion into its zwitterion. The hydrated anion clusters were prepared within a supersonic ion source in which anions were produced by 3-body collisions between thermalized electrons, amino acid-water clusters and argon atoms. The resultant negative ions were then extracted and mass analyzed with a magnetic sector mass spectrometer. Since in the case of $\text{Gly}{\cdot}e^-(H_2O)_n$, no peak was detected for $n = 1-4$, and the hydrated anion cluster peaks appeared for $n \geq 5$, it was concluded that $\text{Gly}{\cdot}e^-(H_2O)_5$ is the smallest hydrated glycine cluster anion to be experimentally seen, for which Gly should be in its zwitterionic (more polar) form. Similar conclusion was derived for the Phe and Trp hydrated cluster anions. However, Johnson and co-workers[191] showed that the glycine molecular anion, $\text{Gly}{\cdot}e^-$, and the hydrated amino acid cluster anions, $\text{Gly}{\cdot}e^-(H_2O)_n$ (n = 1 and 2), with a smaller number of water molecules than those reported by Bowen and co-workers[190] can be created by condensation/charge-exchange method involving reaction of Gly with the negatively charged water cluster anions, $(H_2O)_n{\cdot}e^-{\cdot}\text{Ar}_m$. The analysis of the photoelectron spectra and MP2/aug-cc-pVDZ calculations indicated that $\text{Gly}{\cdot}e^-$ has a diffuse excess electron bound by the high dipole moment isomer of canonical Gly, where the carboxylic OH group points towards the lone pair of electrons of the amino N atom. It was suggested[192] that the minimum cluster size observed by Bowen and co-workers[190] was due to source conditions rather than an indication of the onset of zwitterion formation. Lee and co-workers[193] investigated the Gly·e$^-$(H$_2$O)$_n$ (n = 0−2) anionic clusters with excess electron by calculations with high-level correlated *ab initio* (MP2 and CCSD) and DFT methods (B3LYP and MPW1K) and the aug-cc-pVDZ basis set with additional diffuse functions on the nitrogen atom, and found that for at least $n \leq 2$ the canonical Gly·e$^-$ (H$_2$O)$_n$ clusters are much more favorable than the zwitterion Gly·e$^-$(H$_2$O)$_n$ ones as revealed by Johnson and co-workers in their experiments.[191,192] On the other hand, taking the small barrier heights for isomerization into account it was suggested that the zwitterion Gly·e$^-$ (H$_2$O)$_{0\text{–}2}$ cluster anions may be kinetically unstable for detection by photodetachment in accordance with the Bowen and co-workers experiments.[190] Additional calculations for Gly·e$^-$(H$_2$O)$_n$ indicated the zwitterionic Gly·e$^-$(H$_2$O)$_3$ anion to be the most stable anionic form in the gas phase.[194]

It is interesting to mention here that the complexation of α-amino acid by metal cation or protonated base also favors the intramolecular proton transfer. For example, on the basis of various MS experiments and *ab initio* calculations, the salt-bridge or zwitterion structures were proposed for some complexes of α-amino acids with monovalent (*e.g.*, ArgM$^+$; M$^+$ = K$^+$, Rb$^+$, and Cs$^+$)[195,196] or divalent cations (*e.g.*, AM^{2+}; A = Gly, and Trp; M^{2+} = Ca^{2+}, Sr^{2+}, and Ba^{2+}),[197,198] and for some proton-bound dimers of α-amino acids itself (*e.g.*, Arg·ArgH$^+$, and Pro·ProH$^+$, where one molecule of Arg and Pro has the zwitterion structure and the other one is protonated at the guanidine and secondary amine group, respectively),[199,200] or of α-amino acid and alkylamine (*e.g.*, Pro·RNH$_3^+$, where Pro has the zwitterion structure).[201] Less basic amino acids (Gly) are incapable to form a zwitterion structure by complexation with metal cations or by formation of protonated dimers and even trimers.[202,203] Effects of both alkali metal cations and water molecules on zwitterionic stability of α-amino acids have been mostly studied by E. R. Williams and co-workers.[204]

PERSPECTIVES

Basicities of polyguanides, vinamidines, phosphazenes, and Verkade's bases are known experimentally to be exceptionally high in the gas phase. For simple derivatives, their basicity could be measured,[36,37,54] but the lack of suitable reference compounds renders extremely difficult the measurements for other N-bases having GBs larger than 1100 kJ mol^{-1} (Figure 2). Extrapolations of the correlation line found between the gas-phase and solution (acetonitrile, THF) basicities for the C=N and P=N superbases[36,37,54,57,89] as well as quantum-chemical calculations predict PAs in the range 1100−1400 kJ mol^{-1}. Moreover, theoretical calculations performed by Koppel, Howard, Maksić and their co-workers[88−108] have shown that the more complex and conjugated bases possessing the C=N function may have basicities considerably larger (>1100 kJ mol^{-1}) than those of the strongest organic bases in the current experimental basicity scale.[36,37] These observations indicate that experimental realization of reaction (4) between very strong X=N bases and mineral (*e.g.*, HCl, HBr, HI, HNO$_3$, H$_2$SO$_4$, FSO$_3$H, or HClO$_4$) or organic acids [*e.g.*, (CF$_3$CO)$_n$XH$_m$ or (CF$_3$SO$_2$)$_n$XH$_m$ where X = C, N, O; n = 1, 2, or 3, and m = 1, 2, or 3] seems to be realistic, but still awaits confirmation by gas-phase experimental studies.

As shown in Figure 2, the gas-phase acidity of strong mineral acids (HCl, HBr, HI, H$_2$SO$_4$ and HClO$_4$) are close to the gas-phase basicity of alkali metal oxides (K$_2$O, Na$_2$O, and Cs$_2$O).[26,34,54,114−116] This means that the spontaneous intermolecular proton-transfer according to reaction (13) is thermodynamically possible, although kinetic limitations should be considered. Reactions between HClO$_4$ and K$_2$O, Na$_2$O or Cs$_2$O, and also between Cs$_2$O and HCl, HBr or HI should be observed in the gas phase as exergonic reactions ($\delta_{\mathrm{PT}}\Delta G^\circ < 0$). However, no report of such experiments has been published yet, the major difficulty being the very low volatility of metal oxides. Solely theoretical investigations [B3LYP/6-311++G(d,p)] on feasibility of these kinds of experiments have been recently carried out by Koppel and his group.[205]

$$\mathrm{HX} + \mathrm{M_2O} \rightleftarrows \mathrm{X^-} + \mathrm{M_2OH^+} \qquad (13)$$

Most of the MS techniques, *e.g.*, Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) and high-pressure mass spectrometry (HPMS), widely used for the acidity and basicity measurements[29] are not suitable for studies of the spontaneous intermolecular proton-transfer from a superacidic to a superbasic molecular species. However, modifications of the ICR cell and new propositions for excitation and detection for FTICR-MS offer some possibilities for simultaneous analysis of the positive and negative ions.[206−212] Some other MS techniques such as bipolar time of flight (TOF)-MS for the simultaneous detection in real-time of the positive and negative ions[213,214] quadrupole systems, either as mass filters,[215] quadrupole ion traps,[216] or linear quadrupole ion trap[217,218] may be considered for the 'neutralization' reaction (4) in the gas phase. Other spectroscopic techniques, *e.g.*, IR, MW, NMR, may be suitable to study the intramolecular proton-transfer according to reaction (4), but they should be adapted to compounds of low volatility such as biguanides, vinamidines, phosphazenes, Verkade's bases, alkali metal oxides, *etc*., vapor pressures of which are insufficient considering the current performances of these spectroscopic techniques. Electrochemistry may also be contemplated to study the 'neutralization' reaction in the absence of solvent.[219] However, electrochemistry as well as IR, MW, NMR techniques do not seem to be ready for this kind of experiments. Much more chances are expected from the MS techniques, from the perspective of simultaneous detection of positive and negative ions.

As a concluding remark, the gas-phase spontaneous neutralization reaction (4) between a Brønsted-Lowry neutral superacid AH and a Brønsted-Lowry neutral superbase B seems to be possible, on the basis of physicochemical data. However, technical problems impeding the experimental observation of this reaction are not yet solved, and the question raised in the title is still open.

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SAŽETAK

Kemija prijenosa protona u plinskoj fazi. Da li je reakcija spontane 'neutralizacije' mit ili stvarnost?

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Iz fizikalne kemije je poznato da se proton ne može spontano prenijeti sa plinovitih mineralnih kiselina (HF, HCl, HBr, HI, HNO_3, H_2SO_4, ili $HClO_4$) na plinovitu dušikovu bazu (NH_3, alkilamin, anilin, piridin, amidin, ili gvanidin). Na primjer, potpuni transfer protona s HCl na NH_3, iza kojeg slijedi separacija Cl^- i NH_4^+ zahtijeva više od 500 kJ mol^{-1}. Isto vrijedi za spontani intramolekularni prijenos protona za plinovite amino kiseline, aminofenole i druge amfiprotične spojeve. Na osnovu parametra kiselosti u plinskoj fazi za COOH i parametra bazičnosti u plinskoj fazi za NH_2 (ili druge bazičnije skupine u pokrajnjem lancu), proizlazi da je prijenos protona endoterman ili endergonic. Za arginin, amino kiselinu sa vrlo bazičnom gvanidinskom skupinom, ova razlika je još uvijek veća od 300 kJ mol^{-1}. Jedino solvatacija kiselo-baznog sistema sa neutralnim specijama (npr. jednom ili više molekula vode), kompleksiranjem ionima (npr., ionskm kiselinama ili bazama, metalnim kationima) ili čak elektronima može smanjiti energetsku barijeru i pospješiti transfer protona. Nedavno proširenje ljestvica kiselosti i bazičnosti u plinskoj fazi prema superkiselinama i superbazama, i napredak spektroskopskih tehnika u plinskoj fazi prilagođenih za manje hlapljive organske spojeve predstavljaju perspektivu za praćenje potpunog intermolekularnog prijenosa protona između molekularnih Brønsted-Lowry superkiselina i molekularnih Brønsted-Lowry superbaza.