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Feasibility of the spontaneous gas-phase proton transfer equilibria between neutral Brønsted acids and Brønsted bases

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The computational investigation of interactions of different acid–base pairs regarding the nature and extent of spontaneous proton transfer was carried out at B3LYP/6-311 + G** level. The selected acid–base pairs include the interactions of strong base (K_2O) with acids of different strength ($HClO_4$, HCl, and HF), and strong acid ($HClO_4$) with bases ranging from K_2O (GB = 322.8 kcal/mol) to H_2O (GB = 157.6 kcal/mol). It was shown that spontaneus, unassisted proton transfer can take place in the gas-phase reactions of strong neutral Brønsted acids and bases. The reaction might be barrierless as in case of interactions between strong acids and bases, for example perchloric acid and alkali metal oxides or potassium oxide and halogen hydrides, or involve the encounter complex (hydrogen bonded acid–base cluster), which is separated from ion-pair by the transition state. Copyright © 2008 John Wiley & Sons, Ltd.

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INTRODUCTION

The currently existing experimental gas-phase scale of Brønsted acidities (GA) of neutral acids covers over the 130 kcal/mol range from ethane (GA = 411.7 kcal/mol) and its derivatives to $(n\text{-}C_4F_9SO_2)_2NH$ (GA = 284.1 kcal/mol).[1,2] In a recent series of papers it was suggested that even much higher acidities (close to 200 kcal/mol) could be expected for some modern neutral superacids.[3–8]

The intrinsic basicity scale of the gas-phase Brønsted basicities (GB) covers the range between GB = 35.5 kcal/mol for helium and GB = 264.6 kcal/mol form $EtN{=}P(NMe_2)_2NP(NMe_2)_3$.[9,10] The somewhat outdistanced and not continously populated/covered region of very high basicity ranges up to 337.5 kcal/mol (Cs_2O) and is so far represented with experimentally determined values for such superbases as alkali metal hydroxides, alkali metal oxides, alkali metals, and oxides of alkaline earth metals.[11–14] Extremely strong basicities (ranging from *ca* 240 kcal/mol to *ca* 340 kcal/mol) were predicted for families of ylides, imides, phosphazenes, phosphines, and alkali metal nitrides.[5,10,15–19]

This means that the overlap-area for the basicities of neutral and anionic bases (or the acidites of cationic and neutral Brønsted acids) covers more than 130 kcal/mol range from *ca* 200–230 kcal/mol (acidities of $CB_{11}F_{12}H$ and $CB_{11}(CF_3)_{12}H$)[3]) to *ca* 340 kcal/mol (basicities of Cs_2O[11,14] and K_3N[17]).

Therefore, the realization of the idea[3,4,17,20,21] of spontaneous (without the presence of solvent, additional charged reactants, or applying ionizing radiation, etc.) gas-phase proton-transfer equilibrium between neutral Brønsted acids and neutral base with similar or overlapping values of gas-phase acidity and gas-phase basicity seems to have waited for a practical solution. Some possible ways of its accomplishment have been proposed by some of us as well as by the other groups.[3,14,17–27]

In the present work the investigation of interactions of different acid–base pairs regarding the nature and extent of proton transfer between those partners has been undertaken. The selected pairs include the interactions of a strong base (K_2O) with acids of different strength ($HClO_4$, HCl, and HF), and strong acid ($HClO_4$) with bases ranging from K_2O (GB = 322.8 kcal/mol) to H_2O (GB = 157.6 kcal/mol).

COMPUTATIONAL DETAILS

The computations reported in this work were carried out using Gaussian 03 series of programs.[28] Density functional theory (DFT) calculations with B3LYP hybrid functional which includes Becke's exchange functional and the correlation part due to Lee, Yang, and Parr were used.[29–32] Full geometry optimizations and frequency calculations with vibrational analyses were performed using the 6-311 + G** basis set.[33,34] Calculated unscaled frequencies were used to obtain the thermodynamic parameters (at 298 K) using the standard procedures. This approach has been recently demonstrated[10,35] by some of us to describe with reasonable accuracy the gas-phase basicities and acidities of a wide variety of relatively simple bases and acids. All stationary points were found to be true minima (NImag = 0). Calculated energies, enthalpies, and free energies are given in Table 1.

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Table 1. Energies (*E*), enthalpies (*H*), and free energies (*G*) calculated at B3LYP/6-311 + G** level

	E	*H*	*G*
$HClO_4$	−761.41825	−761.38682	−761.42115
ClO_4^-	−760.93254	−760.91330	−760.94503
HCl	−460.83385	−460.82387	−460.84507
Cl^-	−460.30373	−460.30137	−460.31875
HF	−100.48235	−100.46972	−100.48943
F^-	−99.88869	−99.88633	−99.90285
H_2O	−76.45846	−76.43341	−76.45483
H_3O^+	−76.73107	−76.69293	−76.71595
NH_3	−56.58264	−56.54459	−56.56748
NH_4^+	−56.92032	−56.86705	−56.88947
$(H_2N)_3P{=}NH$	−564.71344	−564.60889	−564.64654
$(H_2N)_3P{=}NH_2^+$	−565.12257	−565.00413	−565.04153
Li_2O	−90.34455	−90.33502	−90.36110
Li_2OH^+	−90.80647	−90.78644	−90.81511
Na_2O	−399.83655	−399.82852	−399.85944
Na_2OH^+	−400.34812	−400.32930	−400.36201
K_2O	−1275.12006	−1275.11233	−1275.14433
K_2OH^+	−1275.65187	−1275.63357	−1275.66868
$H_2O\cdots HClO_4$	−837.89546	−837.83639	−837.87825
$NH_3\cdots HClO_4$	−818.02792	−817.95625	−817.99964
$NH_4^+\cdots ClO_4^-$	−818.02639	−817.95429	−817.99580
$NH_3\cdots HClO_4$[a]	−818.02612	−817.95754	−817.99893
$(H_2N)_3P{=}NH\cdots HClO_4$	−1326.19852	−1326.05883	−1326.11139
$(H_2N)_3P{=}NH_2^+\cdots ClO_4^-$	−1326.19385	−1326.05464	−1326.10932
$Li_2OH^+\cdots ClO_4^-$	−851.94232	−851.90057	−851.94337
$Na_2OH^+\cdots ClO_4^-$	−1161.46255	−1161.42232	−1161.46944
$K_2OH^+\cdots ClO_4^-$	−2036.74514	−2036.70545	−2036.75568
$K_2OH^+\cdots Cl^-$	−1736.13379	−1736.11255	−1736.15249
$K_2OH^+\cdots F^-$	−1375.76158	−1375.74016	−1375.77893

All values in a.u.

[a] Transition state between two complexes.

RESULTS AND DISCUSSION

The proton transfer reaction between acid AH and base B can lead directly to the formation of free ions A^- and BH^+

$$AH + B = A^- + BH^+ \tag{1}$$

Assuming the zero activation energy, for the realization of proton transfer the basicity of B must exceed, or at least be comparable to the basicity of the anionic base A^- (or the acidity of neutral acid AH), $GB(B) \geq GA(AH)$. This is the case for the reaction of perchloric acid and potassium or sodium oxide, where the proton transfer (leading to the free separated ions) is energetically favored and should be spontaneous. Indeed, the geometry optimization starting from assumed encounter geometry of acid and base lead to ion-pair complex of the proton transfer reaction products (Figure 1).

It is important to notice that if the oppositely charged products of the proton-transfer equilibrium (1) might undergo association into the ion-pair as a final product, then the proton transfer reaction should in fact be written as

$$AH + B = A^- \cdots HB^+ \tag{2}$$

and its energetic realization will be much more favorable due to rather significant coulombic stabilization through the interaction of its anionic and cationic products

$$A^- + BH^+ = A^- \cdots HB^+ \tag{3}$$

The extent of that electrostatic stabilization can be calculated as a free energy of reaction (3) which is the difference of free energies of processes (2) and (1). The calculated free energies of reactions (1), (2), and (3) are given in Table 2 together with calculated gas-phase acidities and basicities.

All studied proton transfer reactions involving alkali metal oxides lead to characteristic ion-pair complexes corresponding to proton attached to the oxides oxygen and the alkali metal atoms (bearing considerable positive charge: 0.93–0.97 according to the NBO analysis) electrostatically interacting with anion (Figure 1). The proton transfer from acid to base proceeds without any barrier as evidenced by the geometry optimization leading directly to the product ion pair irrespective to the starting geometry.

Similar results are obtained also for the interaction of perchloric acid and HP1 phosphazene ($(H_2N)_3P{=}NH$)—irrespec-

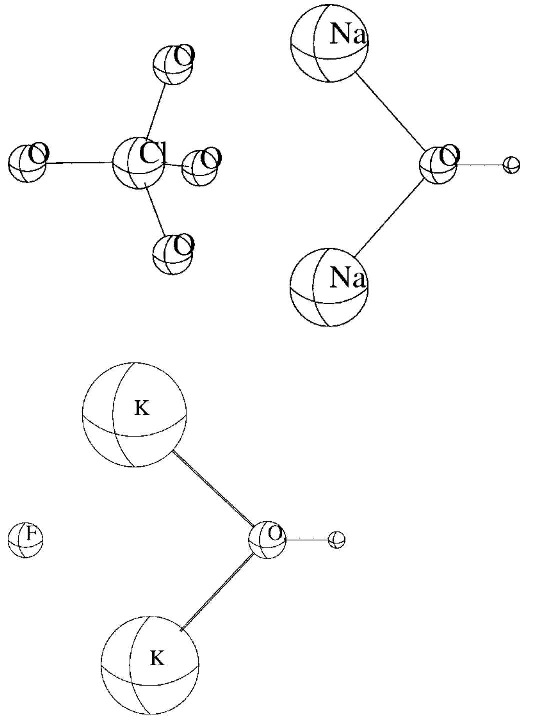

Figure 1. Typical geometries of proton transfer reaction product complexes between acids and alkali metal oxides

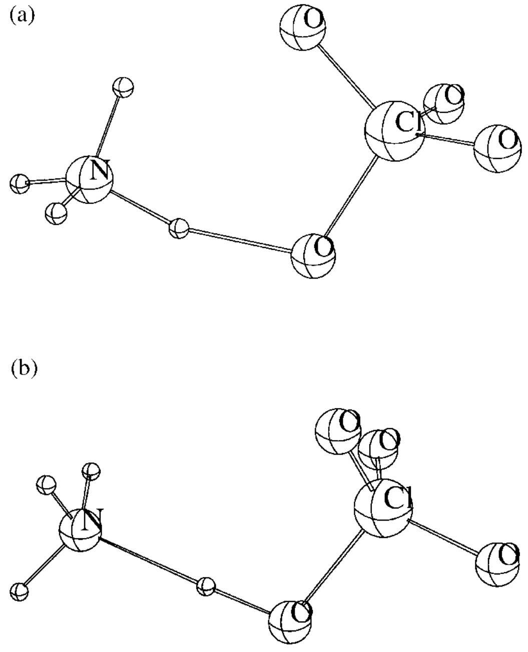

Figure 2. Geometries of complexes between NH_4^+ and ClO_4^- (a), and $HClO_4$ and NH_3 (b). The second complex is by 2.4 kcal/mol more stable as it has two additional N–H··O contacts compared to one in the first complex

tive of the starting geometry the proton transferred ion-pair forms. There are two possible conformations of that ion pair: one with three longer (1.87–2.01 Å) Cl—O···H—N contacts and another with two shorter (*ca* 1.74 Å) ones. The first one (with three contacts) is by 1.3 kcal/mol more stable.

The remaining two bases, ammonia and water, are much weaker compared to previously described ones. As a result, proton transfer reactions of perchloric acid with those bases do not irreversibly proceed to the ion-pair complex. The proton transfer reaction starts with formation of hydrogen bonded encounter complex

$$AH + B = AH\cdots B \qquad (4)$$

and might proceed to the ion-pair complex (NH_3) or not (H_2O).

Table 2. Gas-Phase acidities (GA), basicities (GB), and free energies of reactions (1–3) (ΔG_1, ΔG_2, ΔG_3, all in kcal/mol) of acids HA and bases B, calculated at B3LYP/6-311 + G** level

HA	B	GA	GB	ΔG_1	ΔG_2	ΔG_3
$HClO_4$	H_2O	292.5	157.6	134.9	(−1.4)[a]	−136.3
$HClO_4$	NH_3	292.5	195.8	96.7	−4.5[b]	−103.6
$HClO_4$	$(H_2N)_3P{=}NH$	292.5	241.6	50.9	−27.4	−78.3
$HClO_4$	Li_2O	292.5	278.6	13.9	−101.1	−115.0
$HClO_4$	Na_2O	292.5	309.1	−16.6	−118.5	−101.9
$HClO_4$	K_2O	292.5	322.8	−30.3	−119.3	−89.1
HCl	K_2O	324.0	322.8	1.2	−102.8	−104.0
HF	K_2O	361.8	322.8	39.0	−91.1	−130.1

[a] Corresponds to the formation of hydrogen bonded acid–base complex, that is, free energy change of the reaction (4) as no ion-pair complex was found.

[b] The formation of hydrogen bonded acid–base complex is preferred by 2.4 kcal/mol.

The reaction of the perchloric acid with ammonia leads to the hydrogen bonded acid–base complex, which is only by 2.4 kcal/mol more stable than ion-pair complex. It seems that the former is stabilized by two additional N—H···O interactions while the ion-pair complex has only one additional such contact as the proton transfer from O to N is accompanied by the 60° rotation of the ammonia relative to N···O axis (Figure 2). The reaction barrier between these two complexes (corresponding to the proton transfer and rotation of ammonia) is very small (*ca* 0.2 kcal/mol) and thus the populations of the conformers are defined only by thermodynamics.

The basicity of water (157.6 kcal/mol) is clearly insufficient for proton transfer and so the reaction is finished by the formation of hydrogen-bonded acid–base complex. Independent of the starting geometry only this complex was obtained with very low hydrogen bond energy ($\Delta G(4) = -1.4$ kcal/mol).

Our results are in qualitative accordance with findings of Alkorta *et al.*[26] who predicted that for the proton transfer to take place the difference in the proton affinities of base and the acid anion should not exceed 102 kcal/mol. We have shown (the reaction between perchloric acid and ammonia) that splitting up between proton transfer and hydrogen bond formation can occur at the 97 kcal/mol difference between GA and GB.

CONCLUSIONS

We have shown that spontaneous, unassisted proton transfer can take place in the gas-phase interactions of strong neutral

Brønsted acids and bases. The reaction might be barrierless as in case of interactions between extremely strong superacids and superbases, for example, perchloric acid and alkali metal oxides or potassium oxide and halogen hydrides or involve the encounter complex (hydrogen bonded acid–base cluster), which is separated from ion-pair by the transition state.

However, it should be kept in mind that such proton transfer reactions do not lead to charge separation (i.e., formation of free protonated base and deprotonated acid) despite the fact that in some studied cases (reaction of $HClO_4$ with K_2O or Na_2O) even that reaction would be energetically favorable (relative to separated acid and base). The separation of the ions from the ion-pair is energetically very unfavorable (at least by 80 kcal/mol) and thus the expected product of the proton transfer reaction will be the ion-pair complex.

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