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Gas phase basicity of $X(CH_2)_3Y$(X, Y = OH, NH_2) by the thermokinetic method

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A paper dedicated to the memory of Chava Lifshitz.

Abstract

Gas phase basicity of three homologuous bidentate bases: 1,3-propanediamine, **1**, 1,3-propanolamine, **2**, and 1,3-propanediol, **3**, has been determined by Fourier transform ion cyclotron resonance mass spectrometry. Both, the equilibrium and the thermokinetic methods were used and the results were compared with previous experimental and theoretical determinations. An excellent agreement is generally found between the gas phase basicities given by all the methods if corrections due to entropy variations are taken into account. In particular it is shown that a correction given by the term $\Delta G_a^\circ = -(T - 298)[\langle \Delta_p S^\circ_{298}(B_i)\rangle - \Delta_p S^\circ_{298}(M)]$, where T is an "effective temperature" and $\Delta_p S^\circ$ the protonation entropy of the considered species, should be applied to the thermokinetic determination.

Keywords: Thermokinetic method; Equilibrium method; Bidentate bases; Gas phase basicity; Proton affinity

1. Introduction

Gas phase basicity, GB(M), and proton affinity, PA(M), of a molecule M are quantities of fundamental importance in ion chemistry in general and in mass spectrometry in particular. A number of methods are currently used to derive thermochemical information from experiment [1] and a large compilation of data, obtained by these various procedures, is available [2]. Most of these methods are essentially based on the measurement of the relative basicity of M with respect to a reference bases B_i. This can be done either from determination of the equilibrium constant (equilibrium method [3]) or by measurement of the reaction efficiency (kinetic [4] and thermokinetic [5] methods) of reaction:

$$MH^+ + B_i \rightarrow M + B_iH^+$$

If GB(M) is, in principle, attainable by these procedures at a given temperature T, only methods based on temperature variation can provide the corresponding enthalpic and entropic contributions, i.e., the proton affinity, PA(M), and the "protonation entropy", $\Delta_p S^\circ(M) = S^\circ(MH^+) - S^\circ(M)$. It is the case when the proton transfer equilibrium constant is measured at variable temperature and the desired thermochemical quantities derived from van t'Hoff plots such as from high pressure mass spectrometry (HPMS) experiments [3]. Identical information is theoretically obtained by the "extended" kinetic method which considers dissociation of proton bound heterodimers at different excitation energies [4]. From a methodological point of view, it is crucial to appreciate the limit of applicability of these various experimental techniques. Influence of the experimental parameters, such as temperature and pressure, on the quality of the data provided by the equilibrium method has been emphasized [1–3]. Another important parameter which should be taken into account in evaluating the results, is the protonation entropy, $\Delta_p S^\circ(M)$. Accordingly, it has been recently demonstrated that care should be taken when using the extended kinetic method when $\Delta_p S^\circ(M)$ is significant [4]. Similarly, the results obtained by the variable temperature equilibrium method are subjected to undetermined errors as evidenced from comparison of results obtained by different laboratories [3,4d]. Applications of the thermokinetic method have proven to be reliable in a number of cases [6] but it has never been extended to situations where

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$\Delta_p S^\circ(M)$ is not negligible. It was therefore of interest to investigate, by the thermokinetic method, molecules the protonation of which is known to induce a large entropy change.

Since several decades it has been emphasized that when a molecule M exhibits several basic sites, a strong internal hydrogen bonding may appear in the protonated form MH^+ and can consequently induce an increase of proton affinity. A second consequence is a concomitant decrease of entropy when passing from M to MH^+ due to the more constrained character of the latter. The combination of both effects generally leads to an increase of GB(M) with respect to monodentate bases of comparable polarizability. A number of aliphatic bifunctional molecules are known to undergo a cyclization upon protonation [2,3] and are consequently candidates of choice for the present approach. We choose three homologous aliphatic molecules M previously extensively examined by a number of experimental and theoretical methods, namely 1,3-propanediol, **1**, 1,3-propanediamine, **2**, and 1,3-aminopropanol, **3**. For the purpose of the present study, we submit molecules **1**–**3** to an assay using both the equilibrium and the thermokinetic method in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. Experimental details and parameters necessary to statistical thermodynamic calculations, obtained either from the literature or from the present study, are presented in the following section.

2. Experimental and computational section

FT-ICR experiments were performed on a Bruker CMS 47X mass spectrometer equipped with an external ion source [7]. Molecules M = **1**–**3** were ionised in the external ion source in the chemical ionisation mode using methane as protonating gas. Typical source conditions were: filament current 180 μA, electron energy 100 eV and ionising pulse duration 100 ms. All ions were transferred in the reaction cell located inside the 4.7 T superconducting magnet. After selection of the ions of interest (MH^+), experiments were conducted at a constant pressure of the neutral base B_i in the range 10^{-8} to 10^{-7} mbar as indicated by the ionization gauge (Balzers-IMR-132) located between the high vacuum pump and the cell housing. Reactants were allowed to relax to thermal energy by introducing argon inside the ICR cell at a pressure approximately one order of magnitude greater than the pressure of the neutral base B_i. A relaxation delay of ca. 5 s after the selection of the MH^+ ion was typically used. Subsequently, the selected ions were allowed to react for a variable time with a neutral base. The intensities of the peaks were determined in the frequency domain after Fourier transformation of the corresponding time domain signal. Relative pressures of the neutral molecules were corrected by taking into consideration the sensitivity of the ionisation gauge relative to N_2. Relative sensitivities S_r were estimated according to the method of Bartmess and Georgiadis [8]: $S_r = 0.36\alpha(\text{ahc}) + 0.30$, where α(ahc) is the average molecular polarizability based on atomic hybrid components calculated using the additivity scheme of Miller [9]. The bimolecular rate constants k_{exp} were deduced from the slope of the logarithmic plot of the abundance of reactant ions versus reaction time. The estimated error is ca. 10%. The collision rate constants k_{coll} were calculated according to the trajectory calculations method developed by Su and Chesnavich [10].

The samples, of HPLC grade, were purchased from Sigma–Aldrich (St. Quentin Fallavier, France) and used as received.

The entropy and enthalpy changes associated with temperature variations for molecules M and their protonated form MH^+ were calculated by standard statistical thermodynamic formulae [11]. The necessary parameters were obtained from quantum chemical calculations performed using the Gaussian '03 set of programs [12]. The geometries and the vibrational frequencies of the different species investigated were optimized with the B3LYP functional and the 6-31G(d) basis set. Internal rotations have been treated within the hindered rotor model using, for **1**–**3** and their protonated froms, rotational barriers presented elsewhere [13–15]. After exact calculation of the absolute third law entropies of M and their protonated forms, the following protonation entropies $\Delta_p S^\circ(M) = -22$, -23 and $-14\ \text{J mol}^{-1}\ \text{K}^{-1}$ were calculated for M = **1**–**3**, respectively. The slight differences observed between the present $\Delta_p S^\circ(M)$ values and those presented in references [13–15] are essentially originating from the differences in calculated vibrational frequencies (B3LYP/6-31G(d) against HF/6-31G(d)). The detailed geometries and vibrational frequencies used in the present work are available upon request from the authors.

A non-linear iterative least square procedure has been used to solve parametric equations relating reaction efficiency, RE, to thermochemical quantities (Eq. (5)) (Levenberg–Marquard algorithm implemented in the IGOR Pro package, Wavemetrics Inc.).

3. Results and discussion

3.1. Formulation of the thermokinetic method

The thermokinetic method uses a correlation between the Gibbs free energy and the bimolecular rate of proton transfer reactions involving the molecule of interest M and a reference base B_i. The main hypothesis of the method is to consider that a proton transfer from MH^+ to B_i (reaction (1)) occurs via a single reaction intermediate $[MHB_i]^+$:

$$MH^+ + B_i \underset{k_{-1}}{\overset{k_{coll}}{\rightleftarrows}} [MHB_i]^+ \xrightarrow{k_1} M + B_iH^+ \quad (1)$$

Thus, applying the steady-state approximation to this intermediate, the reaction efficiency RE, i.e., the ratio of the experimental rate constant, k_{exp} determined from the MH^+ decay, to the collision rate constant, k_{coll}, can be expressed by Eq. (2):

$$RE = k_{exp}/k_{coll} = [1 + (k_{-1}/k_1)]^{-1} \quad (2)$$

where k_{-1} and k_1 are unimolecular rate constants for the backward and forward dissociations of the intermediate ion $[MHB_i]^+$ (see Eq. (1)).

By using the canonical thermodynamic formulation of the transition state theory, the reaction efficiency becomes:

$$\mathrm{RE} = [1 + \exp((\Delta_i G_T^{\ddagger})/RT)]^{-1} \quad (3)$$

with $\Delta_i G_T^{\ddagger}$ being the difference in Gibbs free energy between the transition state of the two dissociation channels, i.e., $\Delta_i G_T^{\ddagger} = G_T^{\ddagger\circ}([\mathrm{MHB}_i]^+ \rightarrow \mathrm{M} + \mathrm{B}_i\mathrm{H}^+) - G_T^{\ddagger\circ}([\mathrm{MHB}_i]^+ \rightarrow \mathrm{MH}^+ + \mathrm{B}_i)$ at temperature T. If these transition states are close, in energy and in structure, to the corresponding final states, Eq. (3) may be simplified to:

$$\mathrm{RE} = [1 + \exp((\Delta_i G_T^{\circ})/RT)]^{-1} \quad (4)$$

with

$$\Delta_i G_T^{\circ} = G_T^{\circ}(\mathrm{M}) + G_T^{\circ}(\mathrm{B}_i\mathrm{H}^+) - G_T^{\circ}(\mathrm{MH}^+) - G_T^{\circ}(\mathrm{B}_i)$$

Note that Eq. (3) is only valid for a system in thermal equilibrium at temperature T. Even if the reactants MH^+ and B_i are thermalized, as it is usual in most thermokinetic experiments, the transient intermediate $[\mathrm{MHB}_i]^+$ does not necessarily fulfill this condition, thus, it is more convenient to consider T as an "effective" temperature in all the formulas given therein. This situation is comparable to that encountered in the formulation of the kinetic method [4].

By using the thermokinetic method one may deduce the gas phase basicity $\mathrm{GB}_{298}(\mathrm{M})$ by plotting experimental RE values obtained for a series of reaction (1) involving bases B_i of known basicities, as a function of $\mathrm{GB}_{298}(\mathrm{B}_i)$ and by fitting the data with a parametric function of the type:

$$\mathrm{RE} = a/[1 + \exp(b(c - \mathrm{GB}_{298}(\mathrm{B}_i))] \quad (5)$$

where a is a normalizing factor, b the slope of the curve at RE = 0.5 and c the position of the point RE = 0.5 on a GB scale, these two latter correlation parameters being theoretically related to $1/RT$ and $\mathrm{GB}_{298}(\mathrm{M})$, respectively. A comparable treatment can be applied to the proton affinity, PA(M).

The determination of gas phase basicity GB(M), or proton affinity PA(M), at 298 K needs to develop the quantity $\Delta_i G_T^{\circ}$ into:

$$\Delta_i G_T^{\circ} = \Delta_i H_{298}^{\circ} + \Delta_i H_{298\rightarrow T}^{\circ} - T\Delta_i S_{298}^{\circ} - T\Delta_i S_{298\rightarrow T}^{\circ} \quad (6)$$

where $\Delta_i S_{298}^{\circ}$ is the 298 K entropy change of reaction (1), $\Delta_i S_{298}^{\circ} = S_{298}^{\circ}(\mathrm{M}) + S_{298}^{\circ}(\mathrm{B}_i\mathrm{H}^+) - S_{298}^{\circ}(\mathrm{MH}^+) - S_{298}^{\circ}(\mathrm{B}_i)$, and the terms $\Delta_i H_{298\rightarrow T}^{\circ}$ and $\Delta_i S_{298\rightarrow T}^{\circ}$ are the integral, between 298 and T, of $\Delta_i C_p\,\mathrm{d}T$ and $\Delta_i C_p\,\mathrm{d}T/T$, respectively, with $\Delta C_p = C_p(\mathrm{M}) + C_p(\mathrm{B}_i\mathrm{H}^+) - C_p(\mathrm{MH}^+) - C_p(\mathrm{B}_i)$. By introducing the 298 K gas phase basicities in order to apply the fitting function given by Eq. (5):

$$\Delta_i G_T^{\circ} = \mathrm{GB}_{298}(\mathrm{M}) - \mathrm{GB}_{298}(\mathrm{B}_i) - (T - 298)\Delta_i S_{298}^{\circ} + \Delta_i H_{298\rightarrow T}^{\circ} - T\Delta_i S_{298\rightarrow T}^{\circ} \quad (7)$$

Thus, comparing Eqs. (7) and (5), the parameter c appearing in the latter should be equated to:

$$c = \mathrm{GB}_{298}(\mathrm{M}) - (T - 298)\langle\Delta_i S_{298}^{\circ}\rangle + \langle\Delta_i H_{298\rightarrow T}^{\circ}\rangle - T\langle\Delta_i S_{298\rightarrow T}^{\circ}\rangle \quad (8)$$

where the quoted terms corresponds to the mean values of the relevant quantities for the set of reactions i studied. In other word, when fitting the experimental reaction efficiencies RE versus $\mathrm{GB}_{298}(\mathrm{B}_i)$ points by Eq. (5), the RE = 0.5 value corresponds to the parameter c, i.e., to $\mathrm{GB}_{298}(\mathrm{M})$ plus a correction term $\Delta G_a^{\circ} = -(T - 298)\langle\Delta_i S_{298}^{\circ}\rangle + \langle\Delta_i H_{298\rightarrow T}^{\circ}\rangle - \langle\Delta_i S_{298\rightarrow T}^{\circ}\rangle$. Note that, by introducing the protonation entropies of the reference bases B_i and the molecule of interest M, the mean value of the entropy variation at 298 K may be expressed as $\langle\Delta_i S_{298}^{\circ}\rangle = \langle\Delta_p S_{298}^{\circ}(\mathrm{B}_i)\rangle - \Delta_p S_{298}^{\circ}(\mathrm{M})$.

Similarly, considering RE versus $\mathrm{PA}_{298}(\mathrm{B}_i)$ and fitting the data by a function:

$$\mathrm{RE} = a/[1 + \exp(b(c' - \mathrm{PA}_{298}(\mathrm{B}_i)))] \quad (5')$$

the RE = 0.5 value will correspond to a parameter c' equal to:

$$c' = \mathrm{PA}_{298}(\mathrm{M}) - T\langle\Delta_i S_{298}^{\circ}\rangle + \langle\Delta_i H_{298\rightarrow T}^{\circ}\rangle - T\langle\Delta_i S_{298\rightarrow T}^{\circ}\rangle \quad (8')$$

i.e., to the proton affinity of the molecule shifted by a correction term $\Delta G_a{}^{\circ\prime} = -T\langle\Delta_i S_{298}^{\circ}\rangle + \langle\Delta_i H_{298\rightarrow T}^{\circ}\rangle - T\langle\Delta_i S_{298\rightarrow T}^{\circ}\rangle$. This may be easily shown by writing:

$$\Delta_i G_T^{\circ} = \mathrm{PA}_{298}(\mathrm{M}) - \mathrm{PA}_{298}(\mathrm{B}_i) + \Delta_i H_{298\rightarrow T}^{\circ} - T\Delta_i S_{298}^{\circ} - T\Delta_i S_{298\rightarrow T}^{\circ} \quad (7')$$

As indicated above, evaluation of the thermal correction for enthalpy and entropy, $\Delta H_{298\rightarrow T}^{\circ}$ and $\Delta S_{298\rightarrow T}^{\circ}$ involves integration of the difference in molar heat capacities at constant pressure $\Delta C_p = C_p(\mathrm{M}) + C_p(\mathrm{B}_i\mathrm{H}^+) - C_p(\mathrm{MH}^+) - C_p(\mathrm{B}_i)$ which, because of the structural similarities of $\mathrm{MH}^+ + \mathrm{B}_i$ in one hand and $\mathrm{M} + \mathrm{B}_i\mathrm{H}^+$ in the other, is often assumed to essentially cancel to zero. In such circumstances, Eqs. (8) and (8′) may be approximated by

$$c \sim \mathrm{GB}_{298}(\mathrm{M}) - (T - 298)\langle\Delta_i S_{298}^{\circ}\rangle \quad (9)$$

$$c' \sim \mathrm{PA}_{298}(\mathrm{M}) - T\langle\Delta_i S_{298}^{\circ}\rangle \quad (9')$$

Expressions (8) (or (8′)) and (9) (or (9′)) show clearly that the results given by the thermokinetic method should be dependent on the entropy term $\langle\Delta_i S_{298}^{\circ}\rangle = \langle\Delta_p S_{298}^{\circ}(\mathrm{B}_i)\rangle - \Delta_p S_{298}^{\circ}(\mathrm{M})$. When considering reactions (1) involving a bidentate molecule M, and thus a large and negative $\Delta_p S_{298}^{\circ}(\mathrm{M})$ term, and monodentate bases B_i, with generally small $\Delta_p S_{298}^{\circ}(\mathrm{B}_i)$ values, an overall positive and non-negligible $\langle\Delta_i S_{298}^{\circ}\rangle$ is expected. This obviously leads to significant corrective terms ΔG_a° and $\Delta G_a{}^{\circ\prime}$. In order to assess these conclusions and the validity of relationships (8) (or (8′)) and (9) (or (9′)), the experimental determination of the parameters c and c' obtained from FT-ICR experiments on bidentate bases M = **1**–**3** will be compared with the known protonation thermochemistry of these molecules.

Note that the correction to the Gibbs energy difference due to the true temperature T effect, given by expressions (7) and (7′), are also applicable to the equilibrium and kinetic methods.

3.2. Experimental results

In our thermokinetic experiments, 8–10 reference bases B_i were considered and submitted to proton transfer with proto-

Table 1
Data relevant to proton transfer reactions involving protonated 1,3-propanediol, **1H**$^+$, and reference bases B_i

B_i	GB(B_i)[a]	PA(B_i)[a]	$\Delta_pS(B_i)$[a]	k_{exp}[b]	RE[c]
Pentan-3-one	807.0	836.8	9	2.20	0.10
Cyclohexanone	811.2	841.0	9	4.54	0.19
4-Methylcyclohexanone	813.0	844.9	9	5.6	0.24
4-Heptanone	815.3	845.0	9	8.0	0.38
Di-*n*-butylether	818.3	845.7	17	8.0	0.54
2,4-Dimethylpentan-3-one	820.5	850.3	9	12.1	0.55
Cyclopropylmethylketone	821.8	854.9	2	15.1	0.71
Di-*i*-propylether	828.1	855.5	17	14.1	1.00

[a] GB (kJ/mol) and Δ_pS (J mol^{-1} K^{-1}) values from Ref. [2].
[b] $\times 10^{10}$ (cm^3 molecule^{-1} s^{-1}).
[c] Relative efficiency, RE = $(k_{exp}/k_{coll})/(k_{exp}/k_{coll})_{max}$, k_{coll} calculated using the Su and Chesnavich method (Ref. [10]).

Table 2
Data relevant to proton transfer reactions involving protonated 1,3-propanediamine, **2H**$^+$, and reference bases B_i

B_i	GB(B_i)[a]	PA(B_i)[a]	$\Delta_pS(B_i)$[a]	k_{exp}[b]	RE[c]
Piperidine	921.0	954.0	−2	0.25	0.04
Di-*n*-propylamine	929.3	962.3	−2	0.63	0.10
N-methylpyrrolidine	934.8	965.6	5.6	1.84	0.33
Di-*i*-propylamine	938.6	971.9	−2	3.98	0.70
1-Methylpiperidine	940.1	971.1	5.6	4.63	0.80
Triethylamine	951.0	981.8	5.6	5.72	1.00
2,2,6,6-Tetramethylpiperidine	953.9	987.0	−2	5.97	0.98
Tripropylamine	960.1	991.0	5.6	5.76	0.95

[a] GB (kJ/mol) and Δ_pS (J mol^{-1} K^{-1}) values from Ref. [2].
[b] $\times 10^{10}$ (cm^3 molecule^{-1} s^{-1}).
[c] Relative efficiency, RE = $(k_{exp}/k_{coll})/(k_{exp}/k_{coll})_{max}$, k_{coll} calculated using the Su and Chesnavich method (Ref. [10]).

nated molecules **1**–**3** as depicted by Eq. (1). The thermochemical data tabulated for the reference bases [2] and the reaction efficiencies RE obtained from experimental rate constant determinations are indicated in Tables 1–3.

The thermokinetic graphs where the relative reaction efficiencies, RE, are plotted against the gas phase basicity (or the proton affinity) of the reference bases B_i are illustrated in Figs. 1–3. The

Table 3
Data relevant to proton transfer reactions involving protonated 1,3-aminopropanol, **3H**$^+$, and reference bases B_i

B_i	GB(B_i)[a]	PA(B_i)[a]	$\Delta_pS(B_i)$[a]	k_{exp}[b]	RE[c]
Pyridine	898.1	930.0	2	1.42	0.08
2-Methoxypyridine	902.8	934.7	2	0.54	0.05
N,*N*-dimethylaniline	909.2	941.1	2	0.47	0.04
3-Methylpyridine	911.6	943.4	2	6.0	0.36
Pyrrolidine	915.3	948.3	−2	8.55	0.58
2-Methylpyridine	917.3	949.1	2	7.94	0.48
Methylisopropylamine	919.4	952.4	−2	6.81	0.52
Piperidine	921.0	954.0	−2	9.7	0.74
Di-*n*-propylamine	929.3	962.3	−2	11.6	0.86
Di-*i*-propylamine	938.6	971.9	−2	13.6	1.00

[a] GB (kJ/mol) and Δ_pS (J mol^{-1} K^{-1}) values from Ref. [2].
[b] $\times 10^{10}$ (cm^3 molecule^{-1} s^{-1}).
[c] Relative efficiency, RE = $(k_{exp}/k_{coll})/(k_{exp}/k_{coll})_{max}$, k_{coll} calculated using the Su and Chesnavich method (Ref. [10]).

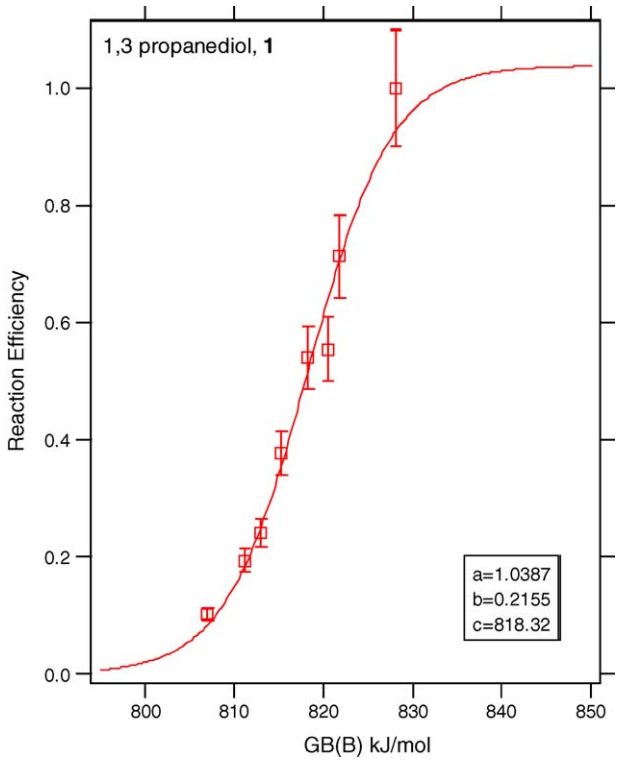

Fig. 1. Normalized reaction efficiency as a function of GB(B_i) for the proton transfer reactions involving protonated 1,3-propanediol: **1H**$^+$ + B_i → **1** + B_iH^+.

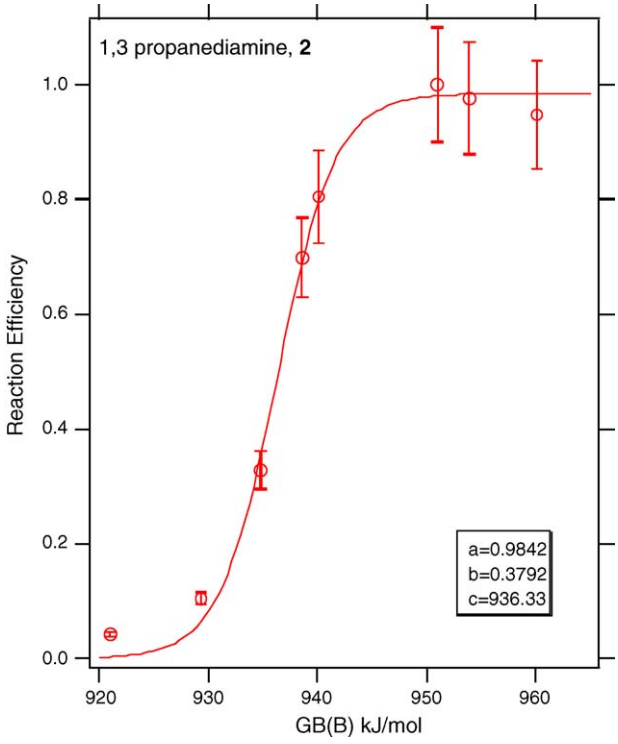

Fig. 2. Normalized reaction efficiency as a function of GB(B_i) for the proton transfer reactions involving protonated 1,3-propanediamine: **2H**$^+$ + B_i → **1** + B_iH^+.

Table 4
Fitting parameters of the thermokinetic plots for molecules **1**–**3**[a]

M	b[b]	c[c]	b'[b]	c'[c]
1,3-Propanediol, **1**	0.215 ± 0.024, [560 ± 60]	818.3 ± 0.6	0.205 ± 0.052, [590 ± 150]	847.9 ± 1.6
1,3-Propanediamine, **2**	0.379 ± 0.034, [320 ± 30]	936.3 ± 0.2	0.334 ± 0.042, [360 ± 50]	967.8 ± 0.5
1,3-Aminopropanol, **3**	0.186 ± 0.042, [650 ± 150]	916.6 ± 1.3	0.174 ± 0.037, [690 ± 150]	949.2 ± 1.3

[a] Errors are standard deviations.
[b] kJ K^{-1}, into bracket the corresponding effective T (K).
[c] kJ/mol.

Table 5
Calculation of the corrective terms ΔG_a°[a] and $\Delta G_a{}^{\circ\prime}$[b] (kJ mol^{-1}) for molecules **1**–**3**

M	Effective temperature, T	$-(T-298)\langle\Delta_i S^\circ_{298\to T}\rangle$	$\langle\Delta_i H^\circ_{298\to T}\rangle$	$-T\langle\Delta_i S^\circ_{298\to T}\rangle$	ΔG_a°
1,3-Propanediol, **1**	560	−8.4[c], −18.9[d]	−1.0	1.1	−8.3, −18.8
1,3-Propanediamine, **2**	320	−0.6[c], −1.1[d]	0.0	0.0	−0.6, −1.1
1,3-Aminopropanol, **3**	650	−5.0[c], −15.5[d]	−0.5	0.6	−4.9, −15.4
M	Effective temperature, T	$-T\langle\Delta_i S^\circ_{298}\rangle$	$\langle\Delta_i H^\circ_{298\to T}\rangle$	$-T\langle\Delta_i S^\circ_{298\to T}\rangle$	$\Delta G_a{}^{\circ\prime}$
1,3-Propanediol, **1**	590	−18.9[c], −42.6[d]	−1.3	1.4	−18.8, −42.5
1,3-Propanediamine, **2**	360	−9.0[c], −18.3[d]	0.1	0.1	−8.8, −18.1
1,3-Aminopropanol, **3**	690	−9.8[c], −30.4[d]	−0.6	0.8	−9.6, −30.2

[a] $\Delta G_a^\circ = -(T-298)\langle\Delta_i S^\circ_{298}\rangle + \langle\Delta_i H^\circ_{298\to T}\rangle - T\langle\Delta_i S^\circ_{298\to T}\rangle$.
[b] $\Delta G_a{}^{\circ\prime} = -T\langle\Delta_i S^\circ_{298}\rangle + \langle\Delta_i H^\circ_{298\to T}\rangle - T\langle\Delta_i S^\circ_{298\to T}\rangle$
[c] Using $\Delta_p S^\circ_{298}$(**1**) = −22 J mol^{-1} K^{-1} (Ref. [13]); $\Delta_p S^\circ_{298}$(**2**) = −23 J mol^{-1} K^{-1} (Ref. [14]); $\Delta_p S^\circ_{298}$(**3**) = −14 J mol^{-1} K^{-1} (Ref. [15]).
[d] $\Delta_p S^\circ_{298}$(**1**) = −62 J mol^{-1} K^{-1} (Ref. [16]); $\Delta_p S^\circ_{298}$(**2**) = −49 J mol^{-1} K^{-1} (Ref. [19]); $\Delta_p S^\circ_{298}$(**3**) = −44 J mol^{-1} K^{-1} (Ref. [19]).

values of the fitting parameters a–c (and a'–c') derived from Eqs. (5) and (5′) are given in Table 4.

In order to derive GB(M) and PA(M) values from the parameters c and c' it is first necessary to estimate the two correction terms ΔG_a° and $\Delta G_a{}^{\circ\prime}$. For this purpose we first assumed that the thermal corrections $\Delta_i H^\circ_{298\to T}$ and $\Delta_i S^\circ_{298\to T}$ were negligible for the monofunctional bases B_i. This is justified by the fact that no significant structural change is expected upon protonation for these molecules and that, consequently, heat capacities differences associated with reaction (1) are negligible. Accordingly, $\langle\Delta_i H^\circ_{298\to T}\rangle$ and $\langle\Delta_i S^\circ_{298\to T}\rangle$ reduce to $\Delta H^\circ_{298\to T}(\mathrm{M}) - \Delta H^\circ_{298\to T}(\mathrm{MH^+})$ and $\Delta S^\circ_{298\to T}(\mathrm{M}) - \Delta S^\circ_{298\to T}(\mathrm{MH^+})$, respectively. As will be seen later this condition is largely fulfilled. Concerning the entropy term $\langle\Delta_i S^\circ_{298}\rangle = \langle\Delta_p S^\circ_{298}(B_i)\rangle - \Delta_p S^\circ_{298}(\mathrm{M})$ we used the tabulated $\Delta_p S^\circ_{298}(B_i)$ values quoted in Tables 1–3 but, for $\Delta_p S^\circ_{298}(\mathrm{M})$, for which large differences are noted in the published values, two extreme values were considered for each molecule M. All the necessary data and the resulting ΔG_a° and $\Delta G_a{}^{\circ\prime}$ values are given in Table 5. It appears from these data that,

Table 6
Gas phase basicities (kJ mol^{-1}) determined from proton transfer equilibrium constant determination using the forward and reverse rate constant ratio method (fr) and the true equilibrium method (eq)

M	B_i	$\Delta G^\circ_{298\,(\mathrm{corrected})}$[a]	GB(B_i)[a]	GB(M)[b]
1,3-Propanediol, **1**	Cyclohexanone (fr)	7.9 ± 1.5[c], 8.7 ± 1.5[d]	811.2	819.1 ± 5[c], 819.9 ± 1.5[d]
	4-Methylcyclohexanone (fr)	818 ± 1.5[c], 8.9 ± 1.5[d]	813.0	821.1 ± 1.5[c], 821.9 ± 1.5[d]
1,3-Propanediamine, **2**	*N*-Methylpyrrolidine (fr)	4.6 ± 1.3[c], 5.1 ± 1.3[d]	934.8	939.4 ± 1.3[c], 939.9 ± 1.3[d]
	Di-*i*-propylamine (fr)	1.4 ± 0.6[c], 1.9 ± 0.6[d]	938.6	940.0 ± 0.6[c], 940.5 ± 0.6[d]
	N-methylpyrrolidine (eq)	3.4 ± 0.7[c], 3.9 ± 0.7[d]	934.8	938.2 ± 0.7[c], 938.7 ± 0.7[d]
	Dimethylbenzylamine (eq)	2.0 ± 0.6[c], 2.5 ± 0.6[d]	937.4	939.5 ± 0.6[c], 939.9 ± 0.6[d]
	Triethylamine (eq)	−11.8 ± 0.3[c], −11.3 ± 0.3[d]	951.0	939.2 ± 0.3[c], 939.7 ± 0.3[d]
1,3-Aminopropanol, **3**	3-Methoxypyridine (fr)	1.6 ± 1.3[c], 2.2 ± 1.3[d]	911.6	913.2 ± 1.3[c], 913.8 ± 1.3[d]
	Pyrrolidine (fr)	−1.4 ± 1.2[c], −0.8 ± 1.2[d]	915.3	913.9 ± 1.2[c], 914.5 ± 1.2[d]
	Methylisopropylamine (eq)	−4.9 ± 0.7[c], −4.3 ± 0.7[d]	919.4	914.5 ± 0.7[c], 915.1 ± 0.7[d]
	Pyrrolidine (eq)	−1.5 ± 1.4[c], −0.9 ± 1.4[d]	915.3	913.8 ± 1.4, 914.4 ± 1.4[d]

[a] According to Refs. [1,2], the FT-ICR equilibrium temperature has been assumed to be 320 K, thus, ΔG°_{298} is corrected following the relationship $\Delta G^\circ_{298} = \Delta G^\circ_{320} - 22\Delta S^\circ_i$ with $\Delta S^\circ_i = \Delta_p S^\circ_{298}(\mathrm{M}) - \Delta_p S^\circ_{298}(B_i)$.
[b] Ref. [2].
[c] Using $\Delta_p S^\circ_{298}$(**1**) = −22 J mol^{-1} K^{-1}; $\Delta_p S^\circ_{298}$(**2**) = −23 J mol^{-1} K^{-1}; $\Delta_p S^\circ_{298}$(**3**) = −14 J mol^{-1} K^{-1} (this work, see computational section).
[d] Using $\Delta_p S^\circ_{298}$(**1**) = −62 J mol^{-1} K^{-1}(Ref. [16]); $\Delta_p S^\circ_{298}$(**2**) = −49 J mol^{-1} K^{-1} (Ref. [19]); $\Delta_p S^\circ_{298}$(**3**) = −44 J mol^{-1} K^{-1} (Ref. [19]).

Table 7
Protonation thermochemistry of molecules **1**–**3**: summary of the data

M	Method	GB(M)[a]	PA(M)[a]	$\Delta_p S^\circ$(M)[b]
1,3-Propanediol, **1**	Equilibrium	826.6 ± 1.7[c]	877.4 ± 2.9[c]	-62 ± 4[c]
		820.1/820.9 ± 1.5[d]		[−22/−62]
	Extended kinetic	823.4[e]	857.6[e]	−6[e]
		820.2[f]	853.2[f]	−2[f]
	Theoretical	812.4[g]	851.5[g]	−22[g]
	Thermokinetic	**826.6 ± 2.5/837.1 ± 5.0**[h]	**866.7 ± 3.6/890.4 ± 6.2**[h]	[−22/−62]
1,3-Propanediamine, **2**	Equilibrium	939.7 ± 1.3[i]	986.5 ± 1.3[h]	-49 ± 2[i]
		938.7[j]	995.6[j]	−81[j]
		942.4[k]/939.6[l]	–	–
		939.0/939.5 ± 0.8[m]	–	[−23/−49]
		939.2/939.7 ± 1.4[d]	–	[−23/−49]
	Extended kinetic	940.4[e]	981.2[e]	−28[e]
		937.5[f]	976.8[f]	−23[f]
		–	982.4[n]	–
		940.6[o]/940.9[o]	974.5[o]/980.5[o]	−5[o]/−24[o]
	Theoretical	936.9[p]	977.7[p]/981.6[q]	−29[p]
	Thermokinetic	**936.9 ± 1.1/937.4 ± 1.9**[h]	**976.6 ± 1.3/986.1 ± 2.2**[h]	[−23/−49]
1,3-Aminopropanol, **3**	Equilibrium	917.9[i]	963.5[i]	−44[i]
		914.5[j]	–	–
		914.2/914.8 ± 1.6[k]	–	[−14/−44]
		913.6/914.2 ± 1.8[d]	–	[−14/−44]
	Extended kinetic	914.6[e]	953.5[e]	−22[e]
	Theoretical	914.8[r]	950.6[r]/952.3[q]	−19[r]
	Thermokinetic	**921.5 ± 3.4/932.0 ± 6.6**[h]	**958.8 ± 3.6/979.5 ± 8.3**[h]	[−14/−44]

[a] KJ mol^{-1}, present results are indicated in bold.
[b] J K^{-1} mol^{-1}, into brackets the two extreme entropy values retained in the correction of GB or PA.
[c] Ref. [16].
[d] This work, from forward and backward reaction rates.
[e] Ref. [17].
[f] Ref. [18].
[g] Ref. [13].
[h] This work, thermokinetic method using the data in Tables 4 and 5, GB(M) $= c - \Delta G_a^\circ$ and PA(M) $= c' - \Delta G_a{}^{\circ\prime}$.
[i] Ref. [19].
[j] Ref. [20].
[k] Ref. [21].
[l] Ref. [22].
[m] This work, from ICR equilibrium constant determination.
[n] Ref. [23].
[o] Ref. [24].
[p] Ref. [14].
[q] Ref. [25].
[r] Ref. [15].

in the range of effective temperature investigated (300–700 K), the thermal correction $\langle \Delta_i H^\circ_{298\rightarrow T}\rangle - T\langle \Delta_i S^\circ_{298\rightarrow T}\rangle$ is always less than 1.5 kJ/mol. Its neglect, and a fortiori that of the contribution of the reference bases, is thus fully justified.

Equilibrium constant of reaction (1) have been also determined for the three target molecules M in the Bruker FT-ICR mass spectrometer. Two methods were used. Direct equilibrium measurement has been done by allowing reaction (1) to occur at fixed partial pressure of the neutrals M and B_i in the FT-ICR cell. The second method consists to measure separately the forward and reverse bimolecular rates of reaction (1) and to take their ratio as the equilibrium constant value. The results of these experiments are presented in Table 6. The temperature of the reacting thermalized species has been assumed to be equal to 320 K as suggested in earlier ICR studies [1,2]. Note that for 1,3-propanediol, **1**, we were unable to attain a correct equilibrium state since a water loss from the MH^+ ions always becomes dominant at long reaction time. Thus, for this molecule, only the estimate of the equilibrium constant based on the measurement of the ratio of experimental forward and reverse rate constants for reaction (1) has been obtained.

3.3. Discussion

Table 7 gathers the GB(M), PA(M) and $\Delta_p S^\circ_{298}$(M) values (M = **1**–**3**) originating from different sources: earlier determinations by the equilibrium and the extended kinetic methods, and the present data resulting from the use of the thermokinetic technique or equilibrium constant determination in the FT-ICR mass spectrometer (values indicated in bold).

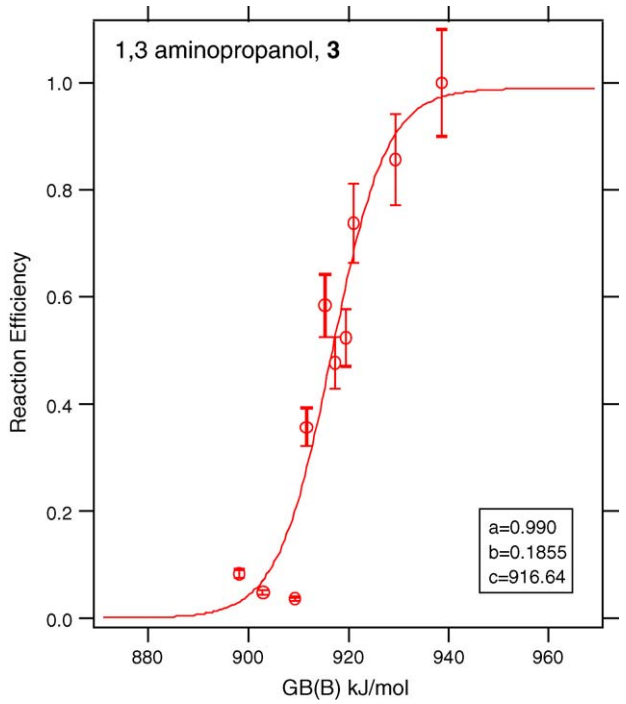

Fig. 3. Normalized reaction efficiency as a function of GB(B_i) for the proton transfer reactions involving protonated 1,3-aminopropanol: $\mathbf{3H}^+ + B_i \rightarrow \mathbf{1} + B_iH^+$.

High pressure variable temperature equilibrium constant determination and FT-ICR forward and reverse rate constant methods give, for 1,3-propanediol, **1**, the largest range of GB values observed here (820–827 kJ/mol). This is perhaps not astonishing considering the experimental difficulties encountered with the handling of the diols under protonation conditions (low vapour pressure and secondary reactions of the protonated forms). This range is however confirmed by the GB(**1**) values given by the extended kinetic method (820–823 kJ/mol). The thermokinetic method gives a figure situated between 827 and 837 kJ/mol, depending on the $\Delta_p S^\circ_{298}$(M) value used (−22 or −62 J mol^{-1} K^{-1}) in the calculation of the corrective term ΔG°_a. The better agreement is obviously obtained when using the lowest absolute value of $\Delta_p S^\circ_{298}$(M) obtained from a theoretical estimate of the absolute third law entropies [13].

Gas phase basicity determinations by the equilibrium methods, either from HPMS or FT-ICR experiments, show an excellent agreement for 1,3-propanediamine, **2** (940 ± 1 kJ/mol). This observation is fully corroborated by the GB(**2**) values (937–941 kJ/mol) obtained from various laboratories by extended kinetic method. Satisfactorily enough, the thermokinetic method provides also a GB(**2**) value (937 kJ/mol) in total agreement with all the above mentioned experimental results and with the G2 theoretical estimate (Table 7). It must be emphasized that, for this molecule, the effective temperature determined from the thermokinetic plot is close to 298 K and that, consequently, the corrective term ΔG°_a, and thus the incidence of the protonation entropy, are negligible.

For 1,3-aminopropanol, **3**, the range of GB values given by the equilibrium methods is relatively narrow (914–918 kJ/mol). The extended kinetic method leads to GB(**3**) = 915 kJ/mol, in clear agreement with these values. The thermokinetic GB(**3**) values are shifted to a slightly higher range of values (921–932 kJ/mol), the corrective action of the ΔG°_a term seems to be to high by ca. 5–16 kJ/mol depending upon the $\Delta_p S^\circ_{298}$(M) value retained (−14 or −44 J mol^{-1} K^{-1}). It should be noted however that the uncertainty on the effective temperature resulting from the thermokinetic fitting (see Table 4) leads to an error on ΔG°_a which point to a correct agreement between the thermokinetic and equilibrium results when the smallest absolute value of $\Delta_p S^\circ_{298}$(M) is used (i.e., $\Delta_p S^\circ_{298}$(M) = −14 J mol^{-1} K^{-1}).

The proton affinites determined by the thermokinetic method are, as expected from consideration of the corrective term $\Delta G_a{}^{\circ\prime}$, more sensitive to the variability of the $\Delta_p S^\circ_{298}$(M) values. This is immediately evidenced by the large range delimited by the PA(M) values calculated using the two sets of $\Delta_p S^\circ_{298}$(M). It is however satisfactory to see that PA(M) obtained from equilibrium constant determination at variable temperature falls precisely between the two extrema of thermokinetic PA(M) given in Table 7.

4. Conclusion

It is shown that the gas phase basicity of a molecule M can, in principle, be determined by the thermokinetic method from a plot of the reaction efficiency of a set of proton transfer reactions $MH^+ + B_i \rightarrow M + B_iH^+$ versus GB(B_i). The reaction efficiency value of 0.5, at an apparent temperature T, corresponds to GB(M) + ΔG°_a where ΔG°_a is a correction term, to a good approximation equal to $-(T - 298)[\langle \Delta_p S^\circ_{298}(B_i)\rangle - \Delta_p S^\circ_{298}(M)]i$. Obviously, the thermokinetic method may provide accurate 298 K gas phase basicity GB_{298}(M) if the apparent temperature T is precisely equal to 298 K or if $\langle \Delta_i S^\circ_{298}\rangle$ is equal to zero. In all the other situations ΔG°_a should be considered, particularly when a large protonation entropy has to be expected.

The aim of the present study was to control that, even in such difficult situations, the thermokinetic method is able to provide meaningful results. For this purpose, GB(M) were determined from the equilibrium method and the thermokinetic method in FT-ICR experiments for bidentate molecules M = 1,3-propanediol, **1**, 1,3-propanediamine, **2**, and 1,3-aminopropanol, **3**. It is demonstrated that, when ΔG°_a is explicitly taken into account, comparison of the GB(M) values obtained by the thermokinetic, the equilibrium or the extended kinetic methods show general agreement, within a few kJ/mol, demonstrating the validity of these different approaches.

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