

# Application of the kinetic method to bifunctional bases MIKE and CID-MIKE test cases

Guy Bouchoux<sup>a,\*</sup>, Fayçal Djazi<sup>b</sup>, Fanny Gaillard<sup>a</sup>, Delphine Vierezet<sup>a</sup>

<sup>a</sup> *Laboratoire des Mécanismes Réactionnels, Department of Chemistry, UMR CNRS 7651, Ecole Polytechnique, F-91128 Palaiseau Cedex, France*

<sup>b</sup> *Département des Sciences Fondamentales, Université de Skikda, BP 26, 21000 Skikda, Algérie, France*

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## Abstract

An assessment of the kinetic method and its applicability to the determination of the basicity of bidentate molecules is done by considering several examples previously studied by equilibrium methods. Selected examples are: 1,2-ethanediol, 1,3-propanediol, glycerol, 1,4-butanediol, 1,2-dimethoxyethane, 2-methoxyethanol methoxyacetone, 1,2-diamino ethane, 1,3-diamino propane and 1,4-diaminobutane. It is generally observed that the orthodox use of the method leads to GB(M), PA(M) and protonation entropy values different from that obtained by the equilibrium method.

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*Keywords:* Kinetic method; Bidentate bases; Gas phase basicity; Proton affinity

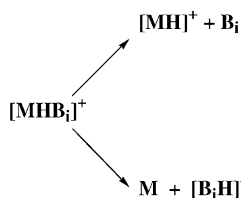
## 1. Introduction

The so-called “kinetic method” has been used to estimate thermochemical data for a wide range of organic molecules for more than twenty years [1], and many of its results are included in recent compilations [2,3]. Basically, the “kinetic method” consists in relating the ratio of the peak intensities associated with two competitive dissociation channels to a difference in thermochemical properties of the corresponding products. For example, the dissociations of the proton-bound dimer  $[\text{MHB}_i]^+$  (Scheme 1): may lead to the differences in gas phase basicities (GB), or pro-

ton affinities (PA), of M and B through the ratio of peak intensities  $[\text{MH}]^+ / [\text{B}_i\text{H}]^+$ . The desired quantitative relationship and the significance of the data are however dependent upon a number of assumptions which are still a matter of debate [4,5]. In particular, critical discussions have been recently raised concerning the consideration of entropy effects in the data analysis [4,5]. The goal of the present study is to examine the applicability of the “kinetic method” to situations known to be associated with important entropy changes upon protonation. Several series of bidentate molecules, such as diols, diethers and diamines, have been studied by equilibrium methods at various temperatures allowing the determination of their proton affinities and their entropy of protonation using van't Hoff plot. Selected examples of these systems are considered here as suitable test cases for an assessment of the “kinetic method”.

\* Corresponding author. Tel.: +33-1-69-33-3400; fax: +33-1-69-33-3041.

E-mail address: [bouchoux@dcmr.polytechnique.fr](mailto:bouchoux@dcmr.polytechnique.fr) (G. Bouchoux).



Scheme 1.

## 2. Experimental

For the purpose of homogeneity, the data selected for the present study were all obtained on a BE tandem mass spectrometer of the type VG ZAB 2F operating in the mass analysed ion kinetic energy (MIKE) mode or in the collision-induced dissociation (CID) mode. Part of the data originate from the works of Holmes and co-workers [5]. The other data were obtained employing the VG ZAB 2F instrument at l'Ecole Polytechnique operating under typical chemical ionization conditions (electron energy: 250 V; emission current: 500  $\mu\text{A}$ ; source temperature: 480 K).

GB and PA values of the reference bases  $\text{B}_i$  are from the Hunter and Lias compilation [2] unless otherwise specified.

## 3. Results and discussion

For the present investigation, we have examined five typical monofunctional molecules (acetone, **1**; butanone, **2**; propylamine, **3**; propanol, **4** and propylcyanide, **5**) and ten, essentially bidentate, compounds (methoxyacetone, **6**; 1,2-dimethoxyethane, **7**; 1,2-ethanediol, **8**; 1,3-propanediol, **9**; glycerol, **10**; 1,4-butanediol, **11**; 1,2-ethanediamine, **12**; 1,3-propanediamine, **13**; 1,4-butanediamine, **14** and 2-methoxyethanol, **15**). For each molecule  $\text{M} = \mathbf{1-15}$ , a series of reference bases  $\text{B}_i$  has been used to produce the relevant proton bound dimer whose spontaneous (MIKE) and CID were treated by the "kinetic method". The corresponding experimental and tabulated data ( $y_i = \ln([\text{MH}]^+ / [\text{B}_i\text{H}]^+)$ ,  $\text{GB}(\text{B}_i)$ ,  $\text{PA}(\text{B}_i)$  and  $\Delta_p S_{298}^\circ(\text{B}_i)$ ) are given in Appendix A, the major results are summarised in Tables 1–3.

Table 1  
Summary of the  $\ln([\text{MH}]^+ / [\text{BH}]^+)$  vs.  $\text{GB}(\text{B}_i)$  correlations ( $\text{GB}(\text{M})$  in  $\text{kJ mol}^{-1}$ ,  $T$  in K)

M	$\text{GB}(\text{M})_{298}^{\text{a}}$	$\text{GB}(\text{M})_{\text{app}}^{\text{b}}$		$\text{GB}(\text{M})_{\text{iso}}^{\text{c}}$	$T^{\text{d}}$		$\Delta G_{\text{d}} = \text{GB}(\text{M})_{298} - \text{GB}(\text{M})_{\text{app}}$		
		MIKE	CID		MIKE	CID	MIKE	CID	Iso
1. $\text{CH}_3\text{COCH}_3$	782.1	781.9	782.0	781.9	327	541	0.2	0.1	0.2
2. $\text{CH}_3\text{COCH}_2\text{CH}_3$	795.6	795.3	793.4	795.6	417	1049	0.3	2.2	0.0
3. <i>n</i> - $\text{C}_3\text{H}_7\text{NH}_2$	883.9	884.7	882.7	885.7	225	722	-0.8	1.2	-1.8
4. <i>n</i> - $\text{C}_3\text{H}_7\text{OH}$	756.1	754.9	755.8	754.9	310	1020	1.2	0.3	1.2
5. <i>n</i> - $\text{C}_3\text{H}_7\text{CN}$	767.7	768.7	768.3	769.1	262	808	-1.0	-0.6	-1.4
6. $\text{CH}_3\text{COCH}_2\text{OCH}_3$	818.7 <sup>e</sup>	813.4	804.9	810.0	312	1034	5.3	13.8	8.7
7. $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$	817.7	814.7	810.9	811.3	268	893	3.0	6.8	6.4
8. $\text{HOCH}_2\text{CH}_2\text{OH}$	773.6	767.8	767.4	756.8	439	613	5.8	6.2	16.8
9. $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$	825.9	817.0	813.0	805.6	600	1005	8.9	12.9	20.3
10. $\text{HOCH}_2\text{CHOHCH}_2\text{OH}$	820.0	809.0	806.0	789.8	486	772	11.0	14.0	30.2
11. $\text{HO}(\text{CH}_2)_4\text{OH}$	855.0	847.4	842.6	822.9	425	826	7.6	12.4	32.1
12. $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	912.5	912.2	902.2	909.1	248	1015	0.3	9.3	3.4
13. $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	940.0	937.6	921.0	929.5	284	1196	2.4	19.0	10.5
14. $\text{H}_2\text{N}(\text{CH}_2)_4\text{N}_2\text{H}$	954.3	957.2	931.5	948.1	402	1522	-2.9	22.8	6.2
15. $\text{HOCH}_2\text{CH}_2\text{OCH}_3$	798.7 <sup>f</sup>	797.2	793.6	796.9	727	1252	0.8	4.4	1.1

<sup>a</sup> From [2], unless otherwise specified.

<sup>b</sup>  $\text{GB}_{\text{app}}(\text{M}) = b/a$  (Eq. (3)).

<sup>c</sup>  $\text{GB}_{\text{iso}} = x_{\text{iso}} + 298 \Delta S^\circ$  (Eqs. (14) and (15)).

<sup>d</sup>  $T = 1/R \cdot a$ , with  $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ .

<sup>e</sup> [9].

<sup>f</sup> The value tabulated in [2] ( $729.8 \text{ kJ mol}^{-1}$ ) is false, it is reexamined here from the original data.

Table 2

Summary of the  $\ln(\text{MH}^+/\text{BH}^+)$  vs.  $\text{PA}(\text{B}_i)$  correlations ( $\text{PA}(\text{M})$  in  $\text{kJ mol}^{-1}$ ,  $T$  in K)

M	$\text{PA}_{298}^{\text{a}}$	$\text{PA}_{\text{app}}^{\text{b}}$		$\text{PA}_{\text{iso}}^{\text{c}}$	$T^{\text{d}}$		$\Delta H_{\text{d}} = \text{PA}_{298} - \text{PA}_{\text{app}}$		
		MIKE	CID		MIKE	CID	MIKE	CID	Iso
1. $\text{CH}_3\text{COCH}_3$	812.0	811.7	811.7	811.6	330	541	0.3	-0.1	0.4
2. $\text{CH}_3\text{COCH}_2\text{CH}_3$	827.3	824.7	822.5	826.1	437	1109	2.6	4.8	1.2
3. $n\text{-C}_3\text{H}_7\text{NH}_2$	917.8	918.9	917.0	919.8	224	720	-1.1	0.8	-2.0
4. $n\text{-C}_3\text{H}_7\text{OH}$	786.5	785.6	787.0	785.1	326	1089	0.9	-0.5	1.4
5. $n\text{-C}_3\text{H}_7\text{CN}$	798.4	799.6	799.2	799.8	258	793	-1.2	-0.8	-1.4
6. $\text{CH}_3\text{COCH}_2\text{OCH}_3$	857.5 <sup>e</sup>	8440	835.7	847.6	303	1015	13.5	21.8	9.9
7. $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$	853.4	844.0	840.3	845.7	250	912	9.4	13.1	7.7
8. $\text{HOCH}_2\text{CH}_2\text{OH}$	815.9	799.0	798.5	800.2	482	693	16.9	17.4	15.7
9. $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$	876.2	846.8	843.0	853.2	592	948	29.4	33.2	23.0
10. $\text{HOCH}_2\text{CHOHCH}_2\text{OH}$	874.8	839.7	836.9	844.2	442	725	35.1	37.9	30.6
11. $\text{HO}(\text{CH}_2)_4\text{OH}$	915.6	878.5	873.9	883.0	403	819	37.1	41.7	32.6
12. $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	951.6	945.2	935.1	948.1	248	1016	6.4	16.5	3.5
13. $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	987.0	970.8	954.1	976.8	286	1205	16.2	32.9	10.2
14. $\text{H}_2\text{N}(\text{CH}_2)_4\text{N}_2\text{H}$	1005.6	989.2	964.6	999.7	404	1517	16.4	41.0	5.9
15. $\text{HOCH}_2\text{CH}_2\text{OCH}_3$	833.7 <sup>f</sup>	827.6	823.8	832.8	769	1340	6.1	9.9	0.9

<sup>a</sup> From [2], unless otherwise specified.<sup>b</sup>  $\text{PA}_{\text{app}} = b/a$  (Eq. (4)).<sup>c</sup>  $\text{PA}_{\text{iso}} = x_{\text{iso}}$ .<sup>d</sup>  $T = 1/R \cdot a$ , with  $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ .<sup>e</sup> [9].<sup>f</sup> The value tabulated in [2] ( $768.8 \text{ kJ mol}^{-1}$ ) is false, it is reexamined here from the original data.

Table 3

Summary of the protonation entropies in  $\text{J K}^{-1} \text{ mol}^{-1}$ 

M	$\Delta_{\text{p}}S^{\circ}(\text{M})^{\text{a}}$	$\overline{\Delta_{\text{p}}S^{\circ}(\text{B}_i)}^{\text{b}}$	$\Delta S^{\circ\text{c}}$	$\Delta S^{\circ}_{\text{iso}}^{\text{d}}$
1. $\text{CH}_3\text{COCH}_3$	8.7	9	-0.3	+0.2
2. $\text{CH}_3\text{COCH}_2\text{CH}_3$	2.0	10	-8.0	-3.1
3. $n\text{-C}_3\text{H}_7\text{NH}_2$	-5.0	-5.7	0.7	-3.9
4. $n\text{-C}_3\text{H}_7\text{OH}$	7.0	5.5	1.5	+1.6
5. $n\text{-C}_3\text{H}_7\text{CN}$	6.0	5.2	0.8	-0.8
6. $\text{CH}_3\text{COCH}_2\text{OCH}_3$	-18.4	5.1	-23.5	-11.8
7. $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$	-11.0	5.5	-16.5	-6.0
8. $\text{HOCH}_2\text{CH}_2\text{OH}$	-33.0	6.5	-39.5	-2.3
9. $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$	-49.0	8.8	-57.8	-10.3
10. $\text{HOCH}_2\text{CHOHCH}_2\text{OH}$	-75.0	7.1	-82.1	-5.4
11. $\text{HO}(\text{CH}_2)_4\text{OH}$	-95.0	4.2	-99.2	-11.5
12. $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	-22.0	-2.0	-20.0	-11.7
13. $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	-49.0	-2.0	-47.0	-21.1
14. $\text{H}_2\text{N}(\text{CH}_2)_4\text{N}_2\text{H}$	-63.0	-2.0	-61.0	-26.2
15. $\text{HOCH}_2\text{CH}_2\text{OCH}_3$	-10.5	6.8	-17.3	-6.8

<sup>a</sup>  $\Delta_{\text{p}}S^{\circ}(\text{M}) = S^{\circ}(\text{MH}^+) - S^{\circ}(\text{M})$  from [2].<sup>b</sup>  $\overline{\Delta_{\text{p}}S^{\circ}(\text{B}_i)}$ : mean values of the  $\Delta_{\text{p}}S^{\circ}(\text{B}_i)$  (see Tables A.1–A.15 for details) from [2].<sup>c</sup>  $\Delta S^{\circ} = \Delta_{\text{p}}S^{\circ}(\text{M}) - \overline{\Delta_{\text{p}}S^{\circ}(\text{B}_i)}$ .<sup>d</sup>  $\Delta S^{\circ}_{\text{iso}} = R \cdot y_{\text{iso}}$  (Eq. (15)) (mean values from the two correlations, GBs and PAs).

### 3.1. Empirical approach

For a series of competitive reactions involving a common molecule  $M$  and different reference bases  $B_i$ , as depicted in Scheme 1, it is generally observed that the natural logarithm of the ion abundance ratio,  $y_i = \ln([\text{MH}]^+ / [\text{B}_i\text{H}]^+)$ , follows linear relationships of the type:

$$y_i = b - a \text{GB}_{298}(\text{B}_i) \quad (1)$$

$$y_i = b' - a' \text{PA}_{298}(\text{B}_i) \quad (2)$$

The intercept of the correlation line with the  $x$  axis leads to what may be called the “apparent” gas phase basicity or proton affinity of the molecule  $M$ , i.e.:

$$\frac{b}{a} = \text{GB}_{\text{app}}(\text{M}) \quad (3)$$

$$\frac{b'}{a'} = \text{PA}_{\text{app}}(\text{M}) \quad (4)$$

thus allowing Eqs. (1) and (2) to be rewritten as

$$y_i = a[\text{GB}_{\text{app}}(\text{M}) - \text{GB}_{298}(\text{B}_i)] \quad (1a)$$

$$y_i = a'[\text{PA}_{\text{app}}(\text{M}) - \text{PA}_{298}(\text{B}_i)] \quad (2a)$$

Most of the published results obtained by the kinetic method assumed that  $\text{GB}_{\text{app}}(\text{M}) = \text{GB}_{298}(\text{M})$  or that  $\text{PA}_{\text{app}}(\text{M}) = \text{PA}_{298}(\text{M})$  depending upon the “entropy cancellation” hypothesis (see Appendix A.2).

Examination of the data presented in Tables 1 and 2 reveals that these assignments are not always correct. The agreement is good for the five monofunctional bases **1–5** both in the MIKE and the CID modes (mean deviation:  $0.8 \text{ kJ mol}^{-1}$  for GB and  $1.3 \text{ kJ mol}^{-1}$  for PA), but for the bifunctional bases **6–15**, the difference between the “apparent” and the 298 K tabulated values reaches ca.  $20 \text{ kJ mol}^{-1}$  for the GBs and  $40 \text{ kJ mol}^{-1}$  for the PAs. The mean deviation appears to be less important for the MIKE’s derived values ( $4.8 \text{ kJ mol}^{-1}$  for GB and  $18.7 \text{ kJ mol}^{-1}$  for PA) than for the CID data ( $12.2 \text{ kJ mol}^{-1}$  for GB and  $26.5 \text{ kJ mol}^{-1}$  for PA). One may note that the discrepancies are larger when using Eqs. (2) and (4), i.e., when correlating  $y_i$  with  $\text{PA}_{298}(\text{B}_i)$ . Another observation is that the deviation

appears to be more pronounced for the molecules bearing the two more distant basic sites. These points will be discussed below.

However, before entering into this discussion, it is convenient to express Eqs. (1) and (2) in a form putting in evidence the above-mentioned deviations. If we define the deviations on the gas phase basicities and the proton affinities by  $\Delta G_d = \text{GB}_{298}(\text{M}) - \text{GB}_{\text{app}}(\text{M})$  and  $\Delta H_d = \text{PA}_{298}(\text{M}) - \text{PA}_{\text{app}}(\text{M})$ , respectively, then the basic relationships become:

$$y_i = a[\text{GB}_{298}(\text{M}) - \text{GB}_{298}(\text{B}_i) - \Delta G_d] \quad (1b)$$

$$y_i = a'[\text{PA}_{298}(\text{M}) - \text{PA}_{298}(\text{B}_i) - \Delta H_d] \quad (2b)$$

At this stage it may be recalled that, for a given species  $X$ , the following relationship holds:

$$\begin{aligned} \text{GB}_{298}(\text{X}) = \text{PA}_{298}(\text{X}) - 298[\text{S}_{298}^\circ(\text{H}^+) \\ + \text{S}_{298}^\circ(\text{X}) - \text{S}_{298}^\circ(\text{XH}^+)] \end{aligned} \quad (5)$$

or, if we define the term  $\Delta_p \text{S}_{298}^\circ(\text{X})$  by the entropy difference  $\text{S}_{298}^\circ(\text{XH}^+) - \text{S}_{298}^\circ(\text{X})$ :

$$\begin{aligned} \text{GB}_{298}(\text{X}) = \text{PA}_{298}(\text{X}) \\ + 298[\Delta_p \text{S}_{298}^\circ(\text{X}) - \text{S}_{298}^\circ(\text{H}^+)] \end{aligned} \quad (5a)$$

Consequently, it turns out that Eq. (1) may be also expressed in terms of proton affinities. Accordingly, Eq. (1b) becomes:

$$\begin{aligned} y_i = a[\text{PA}_{298}(\text{M}) - \text{PA}_{298}(\text{B}_i) \\ + 298[\Delta_p \text{S}_{298}^\circ(\text{M}) - \Delta_p \text{S}_{298}^\circ(\text{B}_i)] - \Delta G_d] \end{aligned}$$

or

$$y_i = a[\text{PA}_{298}(\text{M}) - \text{PA}_{298}(\text{B}_i) + 298 \Delta S^\circ - \Delta G_d] \quad (1c)$$

where  $\Delta S^\circ$  represents the difference  $\Delta_p \text{S}_{298}^\circ(\text{M}) - \Delta_p \text{S}_{298}^\circ(\text{B}_i)$ , i.e., the entropy of the reaction  $\text{B}_i\text{H}^+ + \text{M} \rightarrow \text{B}_i + \text{MH}^+$ . In practice, a set of reactions involving different bases  $B_i$  is used in the linear correlation, consequently  $\Delta S^\circ$  will be more appropriately a mean value obtained by using the average of the tabulated  $\Delta_p \text{S}_{298}^\circ(\text{B}_i)$  values [2].

It is now interesting to compare Eqs. (1) to (2) when  $a = a'$  since it corresponds to most of the observations. Combining (1a) and (2a) it immediately follows that:

$$\begin{aligned} \text{GB}_{\text{app}}(\text{M}) - \text{PA}_{\text{app}}(\text{M}) \\ &= \text{GB}_{298}(\text{B}_i) - \text{PA}_{298}(\text{B}_i) \\ &= 298[\Delta_p S_{298}^\circ(\text{B}_i) - S_{298}^\circ(\text{H}^+)] \\ &= 298 \Delta_p S_{298}^\circ(\text{B}_i) - 32.4 \text{ kJ mol}^{-1} \end{aligned} \quad (6)$$

which simply means that the apparent gas phase basicity and proton affinity are interrelated by the (mean) entropic term associated with the protonation of the reference base  $\text{B}_i$ .

As a corollary, combining (1c) and (2b), a particularly simple relationship is found between the deviations  $\Delta G_d$  and  $\Delta H_d$ :

$$\Delta G_d - \Delta H_d = 298 \Delta S^\circ$$

and consequently:

$$\begin{aligned} \text{GB}_{\text{app}}(\text{M}) - \text{PA}_{\text{app}}(\text{M}) \\ &= \text{GB}_{298}(\text{M}) - \text{PA}_{298}(\text{M}) - 298 \Delta S^\circ \end{aligned} \quad (7)$$

These equalities are correctly verified by our data, since it appears that the differences  $\Delta G_d - \Delta H_d$  are actually the same for the MIKE and CID experiments and that they are closely reproduced by the mean  $298 \Delta S^\circ$  term calculated using the tabulated  $\Delta_p S_{298}^\circ(\text{B}_i)$  and  $\Delta_p S_{298}^\circ(\text{M})$  values (Table 3).

### 3.2. The simplified absolute rate approach

For most of the applications of the kinetic method, the following simplified relationship is used:

$$\ln \frac{[\text{MH}]^+}{[\text{B}_i\text{H}]^+} = \frac{-\Delta G_i^\circ}{RT} \quad (8)$$

where  $\Delta G_i^\circ$  is the Gibbs free energy of the reaction  $\text{B}_i\text{H}^+ + \text{M} \rightarrow \text{B}_i + \text{MH}^+$  at an “effective temperature”  $T$ . This expression results from the application of the absolute rate theory to the competitive reactions  $\text{MHB}_i^+ \rightarrow \text{B}_i\text{H}^+ + \text{M}$  and  $\text{MHB}_i^+ \rightarrow \text{B}_i + \text{MH}^+$  of Scheme 1 (see Appendix B for a summary of the underlying hypothesis supporting Eq. (8)).

Then:

$$y_i = \ln \frac{[\text{MH}]^+}{[\text{B}_i\text{H}]^+} = \frac{1}{RT} [\text{GB}_T(\text{M}) - \text{GB}_T(\text{B}_i)] \quad (8a)$$

For a given species X, the gas phase basicity at a temperature  $T$ ,  $\text{GB}_T(\text{X})$ , is equal to:

$$\begin{aligned} \text{GB}_T(\text{X}) &= \text{GB}_{298}(\text{X}) + [\text{PA}_T(\text{X}) - \text{PA}_{298}(\text{X})] \\ &\quad - T[S_T^\circ(\text{H}^+) - \Delta_p S_T^\circ(\text{X})] \\ &\quad + 298[S_{298}^\circ(\text{H}^+) - \Delta_p S_{298}^\circ(\text{X})] \end{aligned}$$

and consequently the difference in basicity between M and  $\text{B}_i$ :

$$\begin{aligned} \text{GB}_T(\text{M}) - \text{GB}_T(\text{B}_i) \\ &= \text{GB}_{298}(\text{M}) - \text{GB}_{298}(\text{B}_i) + [\text{PA}_T(\text{M}) - \text{PA}_T(\text{B}_i)] \\ &\quad - [\text{PA}_{298}(\text{M}) - \text{PA}_{298}(\text{B}_i)] + T[\Delta_p S_T^\circ(\text{M}) \\ &\quad - \Delta_p S_T^\circ(\text{B}_i)] - 298[\Delta_p S_{298}^\circ(\text{M}) - \Delta_p S_{298}^\circ(\text{B}_i)] \end{aligned} \quad (9)$$

If the temperature  $T$  is not too different from 298 K it may be considered that  $\text{PA}_T(\text{M}) - \text{PA}_T(\text{B}_i) \sim \text{PA}_{298}(\text{M}) - \text{PA}_{298}(\text{B}_i)$  since the heat capacities of  $\text{B}_i + \text{MH}^+$  and  $\text{B}_i\text{H}^+ + \text{M}$  are expected to essentially cancel [2]. Consequently:

$$\begin{aligned} \text{GB}_T(\text{M}) - \text{GB}_T(\text{B}_i) \\ &= \text{GB}_{298}(\text{M}) - \text{GB}_{298}(\text{B}_i) + T[\Delta_p S_T^\circ(\text{M}) \\ &\quad - \Delta_p S_T^\circ(\text{B}_i)] - 298[\Delta_p S_{298}^\circ(\text{M}) - \Delta_p S_{298}^\circ(\text{B}_i)] \end{aligned} \quad (9a)$$

and, if we further assume that  $\Delta_p S_T^\circ(\text{M}) - \Delta_p S_T^\circ(\text{B}_i) \sim \Delta_p S_{298}^\circ(\text{M}) - \Delta_p S_{298}^\circ(\text{B}_i)$ :

$$\begin{aligned} \text{GB}_T(\text{M}) - \text{GB}_T(\text{B}_i) \\ &= \text{GB}_{298}(\text{M}) - \text{GB}_{298}(\text{B}_i) \\ &\quad + (T - 298)[\Delta_p S_{298}^\circ(\text{M}) - \Delta_p S_{298}^\circ(\text{B}_i)] \end{aligned} \quad (9b)$$

Substituting this expression into (8a) we get:

$$y_i = \frac{1}{RT} [\text{GB}_{298}(\text{M}) - \text{GB}_{298}(\text{B}_i) + (T - 298) \Delta S^\circ] \quad (8b)$$

with, again,  $\Delta S^\circ = \Delta_p S_{298}^\circ(\text{M}) - \Delta_p S_{298}^\circ(\text{B}_i)$ , i.e., the entropy of the reactions  $\text{B}_i\text{H}^+ + \text{M} \rightarrow \text{B}_i + \text{MH}^+$ .

Comparing now Eq. (1a) with (8b) it follows that the apparent gas phase basicity of M is given by:

$$GB_{app}(M) = GB_{298}(M) + (T - 298) \Delta S^\circ \quad (10)$$

and consequently, from (1b) we deduce an estimate of the deviation  $\Delta G_d$ :

$$\Delta G_d = -(T - 298) \Delta S^\circ \quad (11)$$

A comparable treatment can be done by considering now the proton affinity  $PA_{298}(M)$  as a target. Using the fact that  $GB_{298}(X) = PA_{298}(X) + 298 [\Delta_p S_{298}^\circ(X) - S_{298}^\circ(H^+)]$  (Eq. (5a)), then Eq. (9) reduces to:

$$\begin{aligned} GB_T(M) - GB_T(B_i) &= [PA_T(M) - PA_T(B_i)] \\ &+ T[\Delta_p S_T^\circ(M) - \Delta_p S_T^\circ(B_i)] \end{aligned} \quad (9c)$$

and, if that  $PA_T(M) - PA_T(B_i) \sim PA_{298}(M) - PA_{298}(B_i)$  and  $\Delta_p S_T^\circ(M) - \Delta_p S_T^\circ(B_i) \sim \Delta_p S_{298}^\circ(M) - \Delta_p S_{298}^\circ(B_i)$ :

$$\begin{aligned} GB_T(M) - GB_T(B_i) &= PA_{298}(M) - PA_{298}(B_i) \\ &+ T[\Delta_p S_{298}^\circ(M) - \Delta_p S_{298}^\circ(B_i)] \end{aligned} \quad (9d)$$

The correlation from (8a) thus becomes:

$$y_i = \frac{1}{RT} [PA_{298}(M) - PA_{298}(B_i) + T \Delta S^\circ] \quad (8c)$$

where  $\Delta S^\circ = \Delta_p S_T^\circ(M) - \Delta_p S_T^\circ(B_i)$ .

Consequently, the apparent proton affinity,  $PA_{app}(M)$ , defined by Eq. (4) and appearing in Eq. (2a), is given by:

$$PA_{app}(M) = PA_{298}(M) + T \Delta S^\circ \quad (12)$$

and the deviation  $\Delta H_d$  observed in Table 2:

$$\Delta H_d = -T \Delta S^\circ \quad (13)$$

It may be noted that Eq. (12) forms the basis of the so-called “extended” (or “full entropy”) analysis by the kinetic method [6]. Accordingly, if this expression is correct (at least) two determinations of  $PA_{app}(M)$  at two different effective temperatures  $T$  allow the estimate of  $PA_{298}(M)$  and  $\Delta S^\circ$ . This treatment may

be done by means of a van't Hoff plot, or by considering the “isothermal” point as discussed below. An assessment of the simplified absolute rate approach will be now detailed in the two following paragraphs, by comparing the predictions of Eqs. (10)–(13) with experiment.

### 3.3. Correlating $y_i$ with $GB_{298}(B_i)$

A plot of  $y_i = \ln([MH]^+/[B_iH]^+)$  as a function of  $GB_{298}(B_i)$  is expected to provide the “effective” temperature  $T$  from the slope of the regression line (parameter  $a$  in Eq. (1),  $a = 1/RT$  in Eq. (8b)) and the apparent gas phase basicity  $GB_{app}(M)$  by the  $x$  intercept ( $b/a = GB_{app}(M)$ , Eq. (3)). As mentioned before, the data collected in Table 1 reveals that  $GB_{app}(M)$  differ from  $GB_{298}(M)$ . The observed deviation,  $\Delta G_d = GB_{298}(M) - GB_{app}(M)$ , is the largest for results obtained under collisional activation, i.e., at high “effective” temperature (Table 1) and for molecules M having a large  $\Delta_p S^\circ(M)$  (Table 3). This is not unexpected since Eq. (11) shows that  $\Delta G_d$  is proportional to both  $T$  and  $\Delta_p S^\circ(M)$  (a component of  $\Delta S^\circ$ ). The comparison between the deviation,  $\Delta G_d$  observed and calculated using Eq. (11) is however not completely satisfactory (Fig. 1). Severe discrepancies appear, when using the CID data, for the molecules M having the largest  $\Delta_p S^\circ(M)$  such as 1,3-propanediol, **9**, glycerol, **10**, 1,4-butanediol, **11**, 1,3-propanediamine, **13** and 1,4-butanediamine, **14**.

If two series of experiments are done, involving two different “effective” temperatures  $T_1$  and  $T_2$ , the two regression lines will intercept at an “isothermal” point. It is evident, from Eq. (8b), that this point correspond to the coordinates:

$$x_{iso} = GB_{298}(M) - 298 \Delta S^\circ \quad (14)$$

$$y_{iso} = \frac{\Delta S^\circ}{R} \quad (15)$$

It is thus theoretically possible to deduce the 298 K gas phase basicity of M,  $GB_{298}(M)$ , and the entropy term  $\Delta S^\circ$  from such double experiments. The applicability of these relationships has been tested here by calculating  $GB_{298}(M)$  from Eq. (14) (denoted  $GB_{iso}(M)$

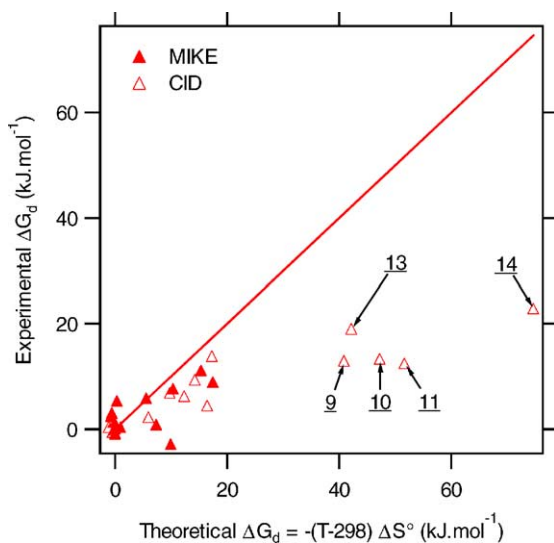


Fig. 1. Experimental deviation  $\Delta G_d = GB_{app}(M) - GB_{298}(M)$  vs. its theoretical estimate  $\Delta G_d = -(T - 298) \Delta S^\circ$  (Eq. (11)).

in Table 1) and  $\Delta S^\circ$  from Eq. (15) (denoted  $\Delta S_{iso}^\circ$  in Table 3) by combining the MIKE and CID data. The  $GB_{iso}(M)$  values from Eq. (14) are reported in Table 1 where a comparison with  $GB_{298}(M)$  is possible. For the five monofunctional compounds 1–5,  $GB_{iso}(M)$  and the tabulated  $GB_{298}(M)$  values agree within a mean deviation of  $1.0 \text{ kJ mol}^{-1}$ . However, considering the bifunctional compounds 6–15, the mean deviation is  $13.6 \text{ kJ mol}^{-1}$ , the worst case is the glycerol molecule for which the deviation is  $30.2 \text{ kJ mol}^{-1}$ .

Concerning the entropy term  $\Delta S^\circ$ , examination of Table 3 shows that the values estimated using Eq. (15) ( $\Delta S_{iso}^\circ = R \cdot y_{iso}$ ) are seriously higher than the  $\Delta S^\circ$  obtained using the tabulated data [2]. These discrepancies are clearly illustrated in Fig. 2.

The deviation may be considerable since it reaches  $87.7 \text{ J mol}^{-1} \text{ K}^{-1}$  for 1,4-butanediol, **11**, i.e.,  $\sim 90\%$  of  $\Delta S^\circ$ . In all the cases, the  $\Delta S^\circ$  calculated from the literature values is more negative than that obtained using Eq. (15) from the  $y_i = f(GB(B_i))$  correlation, or, in other words, the entropy effect actually observed is less pronounced than that expected from the tabulated  $\Delta_p S^\circ$ . Roughly, the experimentally derived  $\Delta S_{iso}^\circ$  represents only 15% of the entropy variation  $\Delta S^\circ$  asso-

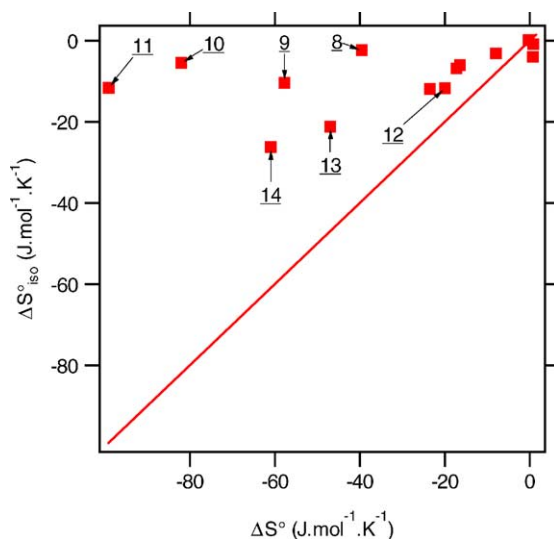


Fig. 2. Experimental entropy term  $\Delta S_{iso}^\circ$ , estimated from the isothermal point (Eq. (15)), vs. the difference in tabulated protonation entropy  $\Delta S^\circ = \Delta_p S_{298}^\circ(M) - \Delta_p S_{298}^\circ(B_i)_{\text{average}}$ .

ciated with reaction  $B_i H^+ + M \rightarrow B_i + M H^+$ . Fig. 2 seems to indicate that the main series, diols **8–11** and diamines **12–14**, behave differently since their representative points appear to fall on two different lines.

A brief comment should be made on the possible errors on the estimate of  $\Delta S^\circ$ . Firstly, since  $\Delta S^\circ$  is a mean value calculated over several  $\Delta_p S^\circ(B_i)$ , it is always associated with a standard deviation, in the presented example this deviation does not exceed  $2 \text{ J mol}^{-1} \text{ K}^{-1}$ . Second, the  $\Delta_p S^\circ(B_i)$  value reported in [2] is often an estimate based on structural similarities of symmetry consideration. Finally, the  $\Delta_p S^\circ(B_i)$  tabulated for the bifunctional compounds may suffer from larger uncertainties due to difficulties in conducting equilibrium measurements at various temperatures. For example, it has recently been found that a theoretical estimate of the  $\Delta_p S^\circ$  of diamines **12–14** leads to values ( $-17, 29, 46 \text{ J mol}^{-1} \text{ K}^{-1}$  [11]) lower than the experimental reported values ( $-22, 49, 63 \text{ J mol}^{-1} \text{ K}^{-1}$ , Table 3). All in all, it seems, however, difficult that these uncertainties may account for the large deviation observed between experimental and theoretical  $\Delta S^\circ$  illustrated in Fig. 2.

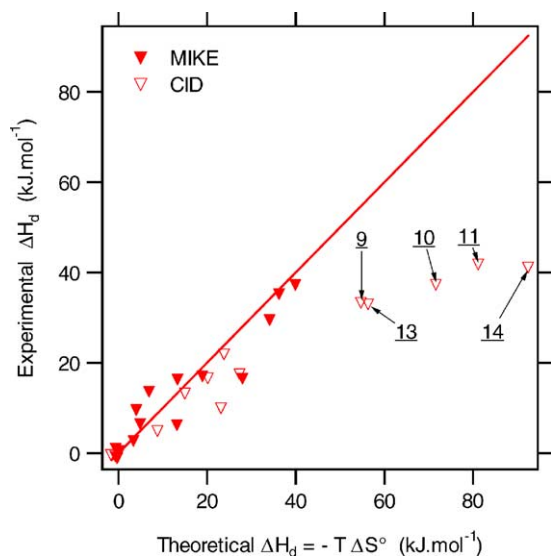


Fig. 3. Experimental deviation  $\Delta H_d = \text{PA}_{\text{app}}(\text{M}) - \text{PA}_{298}(\text{M})$  vs. its theoretical estimate  $\Delta G_d = -T \Delta S^\circ$  (Eq. (13)).

### 3.4. Correlating $y_i$ with $\text{PA}_{298}(\text{B}_i)$

Similarly, a plot of  $y_i = \ln([\text{MH}]^+ / [\text{B}_i\text{H}]^+)$  as a function of  $\text{PA}_{298}(\text{B}_i)$  may be used to obtain the “effective” temperature  $T$  ( $a' = 1/RT$ , Eqs. (2) and (8c)) and the apparent proton affinity  $\text{PA}_{\text{app}}(\text{M})$  by the  $x$  intercept ( $b'/a' = \text{PA}_{\text{app}}(\text{M})$ , Eq. (4)). As suggested by Eq. (12),  $\text{PA}_{\text{app}}(\text{M})$  should be less than  $\text{PA}_{298}(\text{M})$  for most of the studied example since the corresponding  $\Delta S^\circ$  is negative. The observed difference  $\Delta H_d = \text{PA}_{298}(\text{M}) - \text{PA}_{\text{app}}(\text{M})$  is however far from its theoretical value  $-T \Delta S^\circ$  (Eqs. (12) and (13)) as illustrated in Fig. 3. Again, the use of the tabulated  $\Delta_p S^\circ(\text{M})$  in evaluating  $\Delta S^\circ$  leads to an overestimate of the theoretical deviation  $\Delta H_d = -T \Delta S^\circ$ , particularly for 1,4- and 1,3-bifunctional compounds, 9–11, 13 and 14 and for high  $T$  values (i.e., CID data).

Considering now two sets of experiments performed at two “effective” temperatures  $T_1$  and  $T_2$ . Following Eq. (8c), the crossing of the two regression lines should fall at the isothermal point defined by:

$$x'_{\text{iso}} = \text{PA}_{298}(\text{M}) \quad (16)$$

and, again:

$$y_{\text{iso}} = \frac{\Delta S^\circ}{R} \quad (15)$$

Thus, both the proton affinity  $\text{PA}_{298}(\text{M})$  and the entropy term  $\Delta S^\circ$  may be deduced from the two experiments. Note that this procedure is equivalent to the use of Eq. (12) through a van't Hoff-like treatment if several experiments, at different temperatures, are available [6].

The  $\text{PA}_{298}(\text{M})$  calculated using Eq. (16) (denoted  $\text{PA}_{\text{iso}}(\text{M})$  in Table 2) may be compared with the tabulated  $\text{PA}_{298}(\text{M})$  values. We observe trends identical to that which have been noted for  $\text{GB}_{\text{iso}}(\text{M})$ . The agreement between  $\text{PA}_{\text{iso}}(\text{M})$  and  $\text{PA}_{298}(\text{M})$  is correct for compounds 1–5 (mean deviation:  $1.3 \text{ kJ mol}^{-1}$ ) but worse for the bifunctional molecules 6–15 where the mean deviation is  $14.0 \text{ kJ mol}^{-1}$ . It is remarkable that both  $\text{PA}_{\text{iso}}(\text{M})$  and  $\text{GB}_{\text{iso}}(\text{M})$  are shifted to values lower than  $\text{PA}_{298}(\text{M})$  or  $\text{GB}_{298}(\text{M})$  by exactly the same amount (compare  $\Delta G_{\text{iso}}$  in Table 1 to  $\Delta H_{\text{iso}}$  in Table 2). This suggests the participation of a common enthalpic quantity, not included in Eqs. (14) and (16). This point will be developed in the following paragraph. Note that the comparison of the experimental entropic term  $\Delta S_{\text{iso}}^\circ$  with  $\Delta S^\circ$  has been considered previously and will not be repeated here.

### 3.5. The total absolute rate approach

In summary, the preceding paragraphs show that it is difficult to reconcile data obtained by the orthodox implementation of the kinetic method and by equilibrium measurements when the considered molecules present two remote basic sites. The less disappointing situation is the estimate of  $\text{GB}_{298}(\text{M})$  by the direct use of the  $x$  intercept of the  $y_i = f(\text{GB}(\text{B}_i))$  correlation line using the MIKE results. For the considered examples the  $\text{GB}_{298}(\text{M})$  may be “only” underestimated by ca.  $10 \text{ kJ mol}^{-1}$ ! All other comparisons have indicated GBs or PAs underestimated by amounts as large as  $40 \text{ kJ mol}^{-1}$ . Estimates of the entropy term  $\Delta S_{\text{iso}}$  by the isothermal method is also subject to very large difference with the  $\Delta S^\circ$  tabulated data.



Several kinds of phenomenon may explain these discrepancies. The most logical way to account for the deviations observed both in evaluating the entropic and enthalpic quantities is to consider the “exact” relationship:

$$y_i = \ln \frac{[\text{MH}]^+}{[\text{B}_i\text{H}]^+} = \frac{-\Delta G_i^\ddagger}{RT} \quad (17)$$

where  $\Delta G_i^\ddagger$  is the Gibbs free energy difference between the two transition structures  $\text{TS}(\text{MH}^+)$  and  $\text{TS}(\text{B}_i\text{H}^+)$  associated with reactions  $\text{MHB}_i^+ \rightarrow \text{B}_i + \text{MH}^+$  and  $\text{MHB}_i^+ \rightarrow \text{B}_i\text{H}^+ + \text{M}$ , respectively (Scheme 1). The free energy difference  $\Delta G_i^\ddagger$  may be written as:

$$\Delta G_i^\ddagger = \Delta H_i^\ddagger - T \cdot \Delta S_i^\ddagger$$

or, by introducing the proton affinities and the difference in reverse activation enthalpies  $\Delta_R H_i^\ddagger = \Delta_R H^\ddagger(\text{MH}^+) - \Delta_R H^\ddagger(\text{B}_i\text{H}^+)$ :

$$\Delta G_i^\ddagger = [\text{PA}_T(\text{B}_i) - \text{PA}_T(\text{M})] + \Delta_R H_i^\ddagger - T \cdot \Delta S_i^\ddagger$$

Finally, Eq. (17) can be written:

$$y_i = \frac{1}{RT} [\text{PA}_{298}(\text{M}) - \text{PA}_{298}(\text{B}_i) - \Delta_R H_i^\ddagger + T \cdot \Delta S_i^\ddagger] \quad (17a)$$

assuming that  $[\text{PA}_T(\text{M}) - \text{PA}_T(\text{B}_i)] \sim [\text{PA}_{298}(\text{M}) - \text{PA}_{298}(\text{B}_i)]$ .

In fact, Eq. (17a) is a modified version of Eq. (8c), similarly Eqs. (12) and (13) should be expressed as:

$$\text{PA}_{\text{app}}(\text{M}) = \text{PA}_{298}(\text{M}) - \Delta_R H_i^\ddagger + T \cdot \Delta S_i^\ddagger \quad (18)$$

$$\Delta H_d = \Delta_R H_i^\ddagger - T \cdot \Delta S_i^\ddagger \quad (19)$$

The expression of Eq. (17) as a function of gas phase basicities is straightforward:

$$y_i = \frac{1}{RT} [\text{GB}_{298}(\text{M}) - \text{GB}_{298}(\text{B}_i) - \Delta_R H_i^\ddagger + T \cdot \Delta S_i^\ddagger - 298 \Delta S^\circ] \quad (17b)$$

and consequently:

$$\text{GB}_{\text{app}}(\text{M}) = \text{GB}_{298}(\text{M}) - \Delta_R H_i^\ddagger + T \cdot \Delta S_i^\ddagger - 298 \Delta S^\circ \quad (20)$$

$$\Delta G_d = \Delta_R H_i^\ddagger - T \cdot \Delta S_i^\ddagger + 298 \Delta S^\circ \quad (21)$$

Note that, in practice, a linear curve fitting on a series of points  $i$  would deliver thermochemical values where  $\Delta_R H_i^\ddagger$  and  $\Delta S_i^\ddagger$  are averaged, thus mean values of  $\Delta_R H^\ddagger$  and  $\Delta S^\ddagger$  should be more properly used in applying expressions (17)–(21).

Following this line of reasoning the coordinates of the isothermal points should be expressed as:

$$x_{\text{iso}} = \text{GB}_{298}(\text{M}) - \Delta_R H^\ddagger - 298 \Delta S^\circ \quad (22)$$

$$y_{\text{iso}} = \frac{\Delta S^\ddagger}{R} \quad (23)$$

and:

$$x'_{\text{iso}} = \text{PA}_{298}(\text{M}) - \Delta_R H^\ddagger \quad (24)$$

$$y_{\text{iso}} = \frac{\Delta S^\ddagger}{R} \quad (23)$$

for  $y_i = f(\text{GB}_{298}(\text{B}_i))$  and  $y_i = f(\text{PA}_{298}(\text{B}_i))$ , respectively.

These latter relations show that the isothermal points provide only the difference in activation entropy  $\Delta S_{\text{iso}} = \Delta S^\ddagger = S^\circ(\text{TS}(\text{MH}^+)) - S^\circ(\text{TS}(\text{B}_i\text{H}^+))_{\text{averaged}}$ , not the true  $\Delta S^\circ$  (see Fig. 2). Moreover, neither  $\text{GB}_{298}(\text{M})$  or  $\text{PA}_{298}(\text{M})$  could be obtained since the quantity  $\Delta_R H^\ddagger$  is a priori unknown.

The observation of identical deviations  $\Delta G_{\text{iso}} = \text{GB}_{\text{iso}}(\text{M}) - \text{GB}_{298}(\text{M})$  (Table 1) and  $\Delta H_{\text{iso}} = \text{PA}_{\text{iso}}(\text{M}) - \text{PA}_{298}(\text{M})$  (Table 2) is clearly explained by the fact that these differences are precisely equal to the enthalpic term  $\Delta_R H^\ddagger$ .

Finally, Fig. 4 shows that an approximate linear relationship is observed between  $\Delta_R H^\ddagger$  (i.e.,  $\Delta G_{\text{iso}}$  or  $\Delta H_{\text{iso}}$ ) and  $\Delta S^\circ$ . Roughly, if we exclude 1,4-diaminobutane, **14**, from the fit, the experimental points fall along the line  $\Delta_R H^\ddagger = -350 \Delta S^\circ$ .

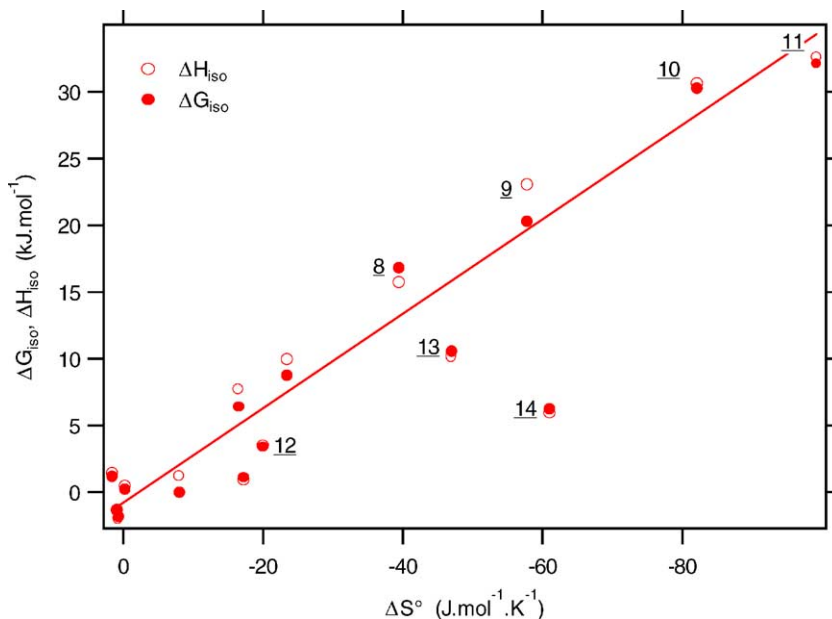


Fig. 4. Experimental deviations  $\Delta G_{\text{iso}} = \text{GB}_{\text{iso}}(\text{M}) - \text{GB}_{298}(\text{M})$  and  $\Delta H_{\text{iso}} = \text{PA}_{\text{iso}}(\text{M}) - \text{PA}_{298}(\text{M})$  (isothermal  $\text{GB}_{\text{iso}}$  and  $\text{PA}_{\text{iso}}$  from Eqs. (14) and (16), respectively) vs. the difference in tabulated protonation entropy  $\Delta S = \Delta_p S_{298}^\circ(\text{M}) - \Delta_p S_{298}^\circ(\text{B}_i)_{\text{average}}$ .

#### 4. Conclusion

The conclusion concerning the use of the kinetic method, in its classical formulation, to obtain true  $\text{PA}_{298}(\text{M})$ ,  $\text{GB}_{298}(\text{M})$  and  $\Delta_p S^\circ(\text{M})$  for bidentate molecules is not optimistic. The graphically obtained  $\text{PA}(\text{M})$ ,  $\text{GB}(\text{M})$  may contain an enthalpic contribution,  $\Delta_R H^\ddagger$ , of unknown magnitude and, seemingly, proportional to  $\Delta S^\circ$ . The graphically obtained entropic term,  $\Delta S^\ddagger$ , is only a small fraction ( $\sim 15\%$ ) of the entropy difference  $\Delta S^\circ$ . The present data confirm and extend previous observations demonstrating similar difficulties [5]. Other experiments and other theoretical treatments should be devised in order to overcome this disappointing situation.

#### Appendix A

##### A.1. Data relevant to the dissociation of protonated adducts $[\text{MHB}_i]^+$

Tables A.1–A.15 contain the various experimental data used in the present study. Each table concerns

one molecule M (M = acetone, **1**; butanone, **2**; propylamine, **3**; propanol; **4**; propylcyanide, **5**; methoxyacetone, **6**; 1,2-dimethoxyethane, **7**; 1,2-ethanediol, **8**; 1,3-propanediol, **9**; glycerol, **10**; 1,4-butanediol, **11**; 1,2-ethanediamine, **12**; 1,3-propanediamine, **13**; 1,4-butanediamine, **14** and 2-methoxyethanol, **15**). For each case, a set of (three to eleven) reference bases  $\text{B}_i$  was used to produce the protonated adduct  $[\text{MHB}_i]^+$  whose unimolecular (MIKE) and CID were studied. Tables A.1–A.15 report the neperian logarithm of the ratio of peak height  $[\text{MH}]^+ / [\text{B}_i\text{H}]^+$  and the tabulated [2] gas phase basicity ( $\text{GB}(\text{B}_i)$  in  $\text{kJ mol}^{-1}$ ), proton affinity ( $\text{PA}(\text{B}_i)$  in  $\text{kJ mol}^{-1}$ ) and protonation entropy ( $\Delta_p S^\circ(\text{B}_i)$  in  $\text{J mol}^{-1} \text{K}^{-1}$ ) of the reference bases  $\text{B}_i$ .

The linear curve fitting procedure implemented in the IgorPro program (WaveMetrics Inc. Lake Oswego) was applied to the sets of  $\ln([\text{MH}]^+ / [\text{B}_i\text{H}]^+)$  vs.  $\text{GB}(\text{B}_i)$  and  $\text{PA}(\text{B}_i)$ . The intercepts of the line with the x axis provided the “apparent” gas phase basicities and proton affinities reported in Tables 1 and 2. Errors on these values are generally less than  $1\text{--}2 \text{ kJ mol}^{-1}$  (using errors on the tabulated GBs and

Table A.1

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, with M: acetone, **1**

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ(B)$ (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> )	
				MIKE	CID
1,4-Dioxane	770.0	797.4	17	4.15	2.63
<i>n</i> -Butylcyanide	771.7	802.4	6	3.52	2.21
<i>i</i> -Propylcyanide	772.8	803.6	5.7	4.35	2.03
<i>t</i> -Butylcyanide	780.2	810.5	6	0.32	0.54
Benzonitrile	780.9	811.5	6	-0.20	0.38
Methylacetate	790.7	821.6	5	-2.58	-2.35
Cyclopentanone	794.0	823.7	9	-4.76	-2.37
Tetrahydrofuranne	794.7	822.1	17	-4.61	-2.90

<sup>a</sup> [2].

Table A.2

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: butanone, **2**

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ(B)$ (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> )	
				MIKE	CID
Cyclohexanone	811.2	841.0	9	-4.61	-2.16
3-Pentanone	807.0	836.8	9	-3.13	-1.56
Ethylacetate	804.7	835.7	5	-2.27	-1.23
Methylvinylketone	802.8	834.7	2	-1.12	-0.59
Cyclopentanone	794.0	823.7	9	0.05	0.01
Methylacetate	790.7	821.6	5	2.16	0.75
Acetone	782.1	512.0	8.7	4.37	1.41

<sup>a</sup> [2].

Table A.3

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: propylamine, **3**

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ(B)$ (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> ) <sup>b</sup>	
				MIKE	CID
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	878.0	912.0	-5.1	4.5	1.3
<i>n</i> -C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub>	886.6	921.5	-8	-2.2	-1.0
<i>n</i> -C <sub>5</sub> H <sub>11</sub> NH <sub>2</sub>	889.5	923.5	-5	-3.5	-1.6
<i>n</i> -C <sub>6</sub> H <sub>13</sub> NH <sub>2</sub>	893.5	927.5	-5	-4.2	-2.0
<i>neo</i> -C <sub>5</sub> H <sub>11</sub> NH <sub>2</sub>	894.0	928.3	-6	-4.8	-1.9
<i>t</i> -C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub>	899.9	934.1	-6	-7.7	-2.3

<sup>a</sup> [2].<sup>b</sup> [5d].

Table A.4

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: propanol, **4**

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ(B)$ (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> ) <sup>b</sup>	
				MIKE	CID
C <sub>2</sub> H <sub>5</sub> OH	746.0	776.4	7	-3.60	-1.16
<i>n</i> -C <sub>4</sub> H <sub>9</sub> OH	758.9	789.2	7	2.15	-
<i>i</i> -C <sub>4</sub> H <sub>9</sub> OH	762.2	793.7	3	2.40	0.75

<sup>a</sup> [2].<sup>b</sup> [5a].

Table A.5

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: propylcyanide, **5**

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ$ (B) (kJ mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> ) <sup>b</sup>	
				MIKE	CID
CH <sub>3</sub> CN	748.0	779.2	4.3	9.4	2.9
C <sub>2</sub> H <sub>5</sub> CN	763.0	794.1	4.7	2.9	1.1
<i>i</i> -C <sub>3</sub> H <sub>7</sub> CN	772.8	803.6	5.7	-1.8	-0.6
<i>n</i> -C <sub>4</sub> H <sub>9</sub> CN	771.7	802.4	6	-1.6	-0.8

<sup>a</sup> [2].<sup>b</sup> [5b].

Table A.6

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: methoxyacetone, **6**

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ$ (B) (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> ) <sup>b</sup>	
				MIKE	CID
Butanone	795.5	827.3	2	7.1	1.0
Cyclopentanone	794.0	823.7	9	7.0	0.96
2-Pentanone	800.9	832.7	2	4.8	0.5
3-Methyl-2-butanone	804.4	836.3	2	3.3	0.2
3-Pentanone	807.0	836.8	9	3.1	0.1
3,3-Dimethyl-2-butanone	810.9 <sup>c</sup>	842.8 <sup>c</sup>	2	1.03	-0.5
Cyclohexanone	811.2	841.0	9	1.06	-0.7
3-Hexanone	811.3	843.2	2	1.15	-0.64
4-Heptanone	815.3	845.0	9	-0.8	-1.20
Cycloheptanone	815.9	845.6	9	-1.0	-1.4
Cyclooctanone	819.6	849.4	9	-2.9	-2.1

<sup>a</sup> [2].<sup>b</sup> [5e].<sup>c</sup> [10].

Table A.7

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: 1,2-dimethoxyethane, **7**

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ$ (B) (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> ) <sup>b</sup>	
				MIKE	CID
2-Pentanone	800.9	832.7	2	-	1.3
Diethylether	801.0	828.4	17 <sup>c</sup>	5.9	1.03
3-Methyl-2-butanone	804.4	836.3	2	4.4	0.95
3-Pentanone	807.0	836.8	9	4.1	0.92
Dipropylether	810.5	837.9	17 <sup>c</sup>	1.8	-0.23
Cyclohexanone	811.2	841.0	9	1.6	0.3
4-Heptanone	815.3	845.0	2	-0.2	-0.50
Cycloheptanone	815.9	845.6	9	-0.4	-0.7
Dibutylether	818.3	845.7	17 <sup>c</sup>	-1.14	-1.11
Cyclooctanone	819.6	849.4	9	-2.9	-1.3

<sup>a</sup> [2].<sup>b</sup> [5e].<sup>c</sup> A better correlation is observed between ln(MH<sup>+</sup>/BH<sup>+</sup>) and GB(B) than with PA(B); in this latter case, the points are shifted toward too lower PA value, probably due to a too large  $\Delta_p S^\circ$ (B).

Table A.8

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: 1,2 ethanediol, **8**

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ$ (B) (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> )	
				MIKE	CID
2-Methyl-1-propanol	762.2	793.7	3	1.60	1.30
Propylcyanide	767.7	798.4	6	-0.12	-0.50
<i>n</i> -Butylcyanide	771.7	802.4	6	-1.08	-0.93
Cyclopropylcyanide	775.5	808.2	6	-2.07	-1.35

<sup>a</sup> [2].

Table A.9

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: 1,3-propanediol, **9**

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ$ (B) (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> )	
				MIKE	CID
3-Pentanone	807.0	836.8	9	2.35	0.64
3,3-Dimethyl-2-butanone	810.9	842.8	2	1.26	0.20
Methylcyclopropanecarboxylate	811.2	842.1	5	1.45	0.18
<i>t</i> -Butylmethylether	812.4	841.6	11	0.49	0.74
4-Heptanone	815.3	845.0	9	0.01	-0.60
Dibutylether	818.3	845.7	17	-0.62	-0.79
2,4-Dimethyl-3-pentanone	820.5 <sup>b</sup>	850.3 <sup>b</sup>	2	-0.75	-1.14
Cyclopropylmethylketone	821.8	853.6	2	-0.49	-0.95
Di-isopropylether	828.1	855.5	17	-2.13	-1.65

<sup>a</sup> [2].<sup>b</sup> [10].

Table A.10

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: glycerol, **10**

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ$ (B) (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> )	
				MIKE	CID
Methylpropionate	799.2	830.2	5	2.44	0.92
2-Pentanone	800.9	832.7	2	1.90	0.86
3-Methylbutanone	804.4	836.3	2	1.20	0.20
3-Pentanone	807.0	836.8	9	0.80	0.02
3,3-Dimethyl-2-butanone	810.9 <sup>b</sup>	842.8 <sup>b</sup>	2	-0.70	-1.06
<i>t</i> -Butylmethylether	812.4	841.6	11	-0.97	-0.38
4-Heptanone	815.3	845.0	9	-1.70	-2.08
Dibutylether	818.3	845.7	17	-2.05	-1.73

<sup>a</sup> [2].<sup>b</sup> [10].

PAs of  $\pm 4$  kJ mol<sup>-1</sup> and errors on the experimental ln([MH]<sup>+</sup>/[B<sub>i</sub>H]<sup>+</sup>) of 20%). The largest error were observed in the determination of the GB<sub>app</sub> and PA<sub>app</sub> of 1,3-propanediamine ( $\pm 3.6$  kJ mol<sup>-1</sup>) and 1,4-butanediamine ( $\pm 2.9$  kJ mol<sup>-1</sup>). Special comments are included, when necessary, as footnotes in the corresponding table.

## A.2. Summary of the hypothesis inherent to the kinetic method

### A.2.1. H1: ratio of rate constants/ratio of peak intensities

The basis of the application of the absolute rate theory to the kinetic method lies in the formal kinetic

Table A.11

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: 1,4-butanediol, **11**

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ$ (B) (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> )	
				MIKE	CID
2-Pentene-4-one	832.5	864.3	2	4.10	1.60
Pyrrrole	843.8	875.4	2.8	1.62	0.26
Mesityloxiide	846.9	878.7	2	-0.55	-1.07
Dicylopropylketone	850.6	880.4	9	-0.22	-0.95
Dimethylsulfoxide	853.7	884.4	5.8	-2.50	-1.90
<i>N,N</i> -Dimethylformamide	856.6	887.5	5	-2.20	-2.20
<i>N</i> -Methylacetamide	857.6	888.5	5	-3.00	-2.50
<i>N</i> -Ethylacetamide	867.0	898.0	5	-	-2.90
2-Chloropyridine	869.0	900.9	2	-	-4.00

<sup>a</sup> [2].

Table A.12

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: 1,2-ethanediamine, **12**

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ$ (B) (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> ) <sup>b</sup>	
				MIKE	CID
NH(CH <sub>3</sub> ) <sub>2</sub>	896.5	929.5	-2	7.52	0.74
NH(CH <sub>3</sub> )(C <sub>2</sub> H <sub>5</sub> )	909.2	942.2	-2	1.72	-0.69
NH(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	919.4	952.4	-2	-3.69	-2.20
NH( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	929.3	962.3	-2	-8.26	-3.04

<sup>a</sup> [2].<sup>b</sup> [5c].

Table A.13

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: 1,3-propanediamine, **13**

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ$ (B) (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> ) <sup>b</sup>	
				MIKE	CID
NH(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	919.4	952.5	-2	-	0.34
NH( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	929.3	962.3	-2	3.90	-0.80
NH( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	935.3	968.5	-2	0.09	-1.80
NH( <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	938.6	971.9	-2	0.70	-2.20
NH( <i>n</i> -C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub>	940.7 <sup>c</sup>	974.1 <sup>c</sup>	-2	-2.30	-2.50
NH( <i>s</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	947.5 <sup>c</sup>	980.7 <sup>c</sup>	-2	-3.90	-2.9
NH( <i>n</i> -C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub>	948.2 <sup>c</sup>	981.5 <sup>c</sup>	-2	-4.50	-2.70

<sup>a</sup> [2].<sup>b</sup> [5c].<sup>c</sup> Reconsidered from data of [5c].

treatment of the competition between two reactions from a common precursor [1]. It is easily demonstrated that, at any observation time, the abundance ratio of the two competitive products is equal to the ratio of

both rate constants. In the particular, case of an isolated specie such as the adduct [MHB<sub>i</sub>]<sup>+</sup> with internal energy *E* dissociating into B<sub>i</sub> + MH<sup>+</sup> and B<sub>i</sub>H<sup>+</sup> + M (Scheme 1) at an observation time *t*, this means that

Table A.14

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: 1,4-butanediamine, 14

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ$ (B) (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> ) <sup>b</sup>	
				MIKE	CID
NH(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	919.4	952.5	-2	-	1.10
NH( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	929.3	962.3	-2	-	0.30
NH( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	935.3	968.5	-2	6.10	-0.40
NH( <i>i</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	937.4 <sup>c</sup>	970.8 <sup>c</sup>	-2	5.60	-0.50
NH( <i>n</i> -C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub>	940.7 <sup>c</sup>	974.1 <sup>c</sup>	-2	4.40	-1.10
NH( <i>n</i> -C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub>	948.2 <sup>c</sup>	981.5 <sup>c</sup>	-2	2.30	-1.30

<sup>a</sup> [2].

<sup>b</sup> [5c].

<sup>c</sup> Reconsidered from data of [5c].

Table A.15

Thermochemical data for reference bases B<sup>a</sup> and natural logarithm of the experimental peak intensity ratio MH<sup>+</sup>/BH<sup>+</sup>, M: 2-methoxyethanol, 15

B	GB(B) (kJ mol <sup>-1</sup> )	PA(B) (kJ mol <sup>-1</sup> )	$\Delta_p S^\circ$ (B) (J mol <sup>-1</sup> )	ln(MH <sup>+</sup> /BH <sup>+</sup> )	
				MIKE	CID
Acetone	782.1	812.0	8.7	2.20	0.74
Butanone	795.5	827.3	2	0.73	0.31
Cyclopentanone	794.0	823.7	9	0.63	0.24
2-Pentanone	800.9	832.7	2	-0.63	-0.55
Diethylether	801.0	828.4	17	-0.25	-0.60
3-Methyl-2-butanone	804.4	836.3	2	-1.85	-1.70

<sup>a</sup> [2].

the ratio of ion numbers is equal to the ratio of the corresponding microcanonical rate constants:

$$\frac{[\text{MH}]_{E,t}^+}{[\text{B}_i\text{H}]_{E,t}^+} = \frac{k_E(\text{MH}^+)}{k_E(\text{B}_i\text{H}^+)}$$

The first hypothesis is to assume that  $[\text{MH}]_{E,t}^+ / [\text{B}_i\text{H}]_{E,t}^+$  is simply given by the ratio of peak intensities  $[\text{MH}]_{\text{exp}}^+ / [\text{B}_i\text{H}]_{\text{exp}}^+$  obtained from mass spectrometric experiments. This suppose no mass or kinetic energy discrimination effect, identical observation time (and time window) for both product ions. Obviously, a true competition should prevail, i.e., there are no successive dissociations and no participation of the non-competitive region where only the lowest energy process is occurring.

### A.2.2. H2: microcanonical/canonical rate constants

Thermochemical quantities such as GB, PA and  $\Delta_p S^\circ$  concern a population of species in thermal equilibrium at a given temperature  $T$  while the dissociations of the isolated  $[\text{MHB}_i]^+$  ions is dependent on its internal energy  $E$ . The canonical rate constant  $k_T$  is related to its microcanonical counterpart  $k_E$  by:

$$k_T = \int k_E \cdot P(E, T) dE$$

where  $P(E, T)$  represents the distribution of the reacting species at temperature  $T$ . Using the general form of the microcanonical rate constant:

$$k_E = \sigma \cdot \frac{G^\ddagger(E - E0)}{h \cdot N(E)}$$

with  $\sigma$  a statistical factor,  $G^\ddagger(E - E_0)$  the sum of rovibrational states of the transition structure,  $h$  the Planck constant and  $N(E)$  the rovibrational density of states of the dissociating specie, and a normalized Maxwell–Boltzmann distribution  $P(E, T)$ , it follows that:

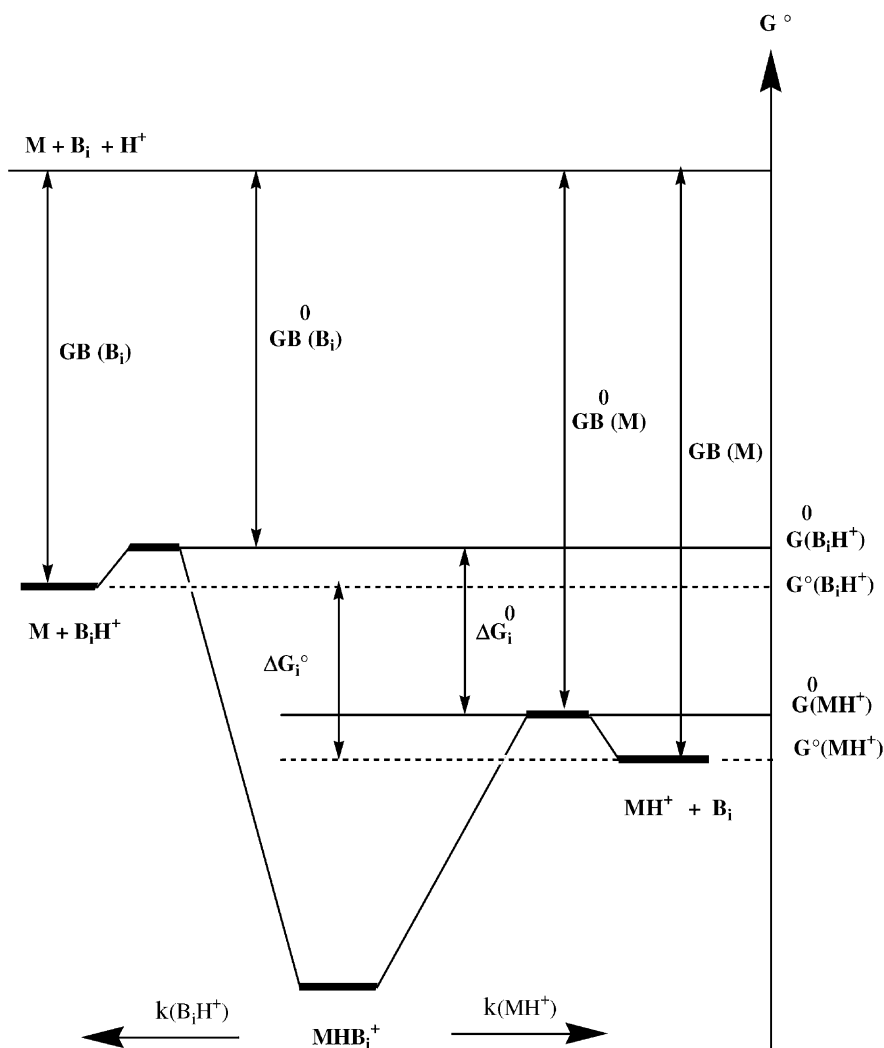
$$k_T = \left( \frac{k_B \cdot T}{h} \right) \exp \left( \frac{-G^\ddagger}{RT} \right)$$

where  $k_B$  is the Boltzmann constant,  $R$  the gas constant and  $\Delta G^\ddagger$  the free activation energy of the considered reaction [7].

The usual hypothesis of the kinetic method is to consider that the experimental ratio of peak intensities  $[\text{MH}]_{\text{exp}}^+ / [\text{B}_i\text{H}]_{\text{exp}}^+$  is equal to the ratio of the corresponding canonical rate constants  $k_T(\text{MH}^+) / k_T(\text{B}_i\text{H}^+)$ , i.e.:

$$\frac{[\text{MH}]_{\text{exp}}^+}{[\text{B}_i\text{H}]_{\text{exp}}^+} = \exp \left( \frac{-\Delta G_i^\ddagger}{RT} \right)$$

where  $\Delta G_i^\ddagger$  is the Gibbs free energy difference between the two transition structures  $\text{TS}(\text{MH}^+)$



Scheme 2.



and  $\text{TS}(\text{B}_i\text{H}^+)$  associated with reactions  $\text{MHB}_i^+ \rightarrow \text{B}_i + \text{MH}^+$  and  $\text{MHB}_i^+ \rightarrow \text{B}_i\text{H}^+ + \text{M}$ , respectively

The principal difficulties are that (i) the equality between the microcanonical ratio  $k_E(\text{MH}^+)/k_E(\text{B}_i\text{H}^+)$  and the canonical ratio  $k_T(\text{MH}^+)/k_T(\text{B}_i\text{H}^+)$  is not obvious and that (ii) the isolated  $[\text{MHB}_i]^+$  ions are not generally in thermal equilibrium and that the canonical expression may be hardly applicable. One way to circumvent these problems is to define an “effective” temperature  $T^*$  and thus to write:

$$\frac{[\text{MH}]_{\text{exp}}^+}{[\text{B}_i\text{H}]_{\text{exp}}^+} = \exp\left(\frac{-\Delta G_i^\ddagger}{RT^*}\right) \quad (\text{A.1})$$

Discussions concerning the meaning of the effective temperature are available in [8].

#### A.2.3. H3: activation/reaction free energies

The question is now to relate the free energy difference  $\Delta G_i^\ddagger$  to a measurable quantity such as the gas phase basicity.

Considering Scheme 2, it is clearly expected that  $\Delta G_i^\ddagger = G_i^\ddagger(\text{MH}^+) - G_i^\ddagger(\text{B}_i\text{H}^+)$  may be different from the gas phase basicity difference  $\Delta G_i^\circ = G^\circ(\text{MH}^+) - G^\circ(\text{B}_i\text{H}^+) = \text{GB}(\text{B}_i) - \text{GB}(\text{M})$ . One may write, for example,  $\Delta G_i^\ddagger = \Delta G_i^\circ + \Delta_R G_i^\circ$  where the latter term account for the difference in the reverse free energy barriers.

In order to apply the kinetic method, another hypothesis consists to consider that the term  $\Delta_R G_i^\circ$  is negligible. This situation is expected to arise if both dissociation reactions are simple cleavage processes. Thus, Eq. (A.2):

$$\frac{[\text{MH}]_{\text{exp}}^+}{[\text{B}_i\text{H}]_{\text{exp}}^+} = \exp\left(\frac{-\Delta G_i^\circ}{RT^*}\right) \quad (\text{A.2})$$

has been, and still is, widely used to deduce  $\text{GB}(\text{M})$  and  $\Delta_p S^\circ(\text{M})$ .

#### A.2.4. H4: free energy/enthalpy

Finally, a last simplification has been often used. Since  $\Delta G_i^\circ = \Delta H_i^\circ - T \cdot \Delta S_i^\circ$  and if the entropy variation associated with the reaction  $\text{B}_i\text{H}^+ + \text{M} \rightarrow$

$\text{B}_i + \text{MH}^+$  is expected to be negligible, then Eq. (A.2) becomes:

$$\frac{[\text{MH}]_{\text{exp}}^+}{[\text{B}_i\text{H}]_{\text{exp}}^+} = \exp\left(\frac{-\Delta H_i^\circ}{RT^*}\right) \quad (\text{A.3})$$

This situation has been supposed to apply when base M and  $\text{B}_i$  possess structural similarities. We note however that this is not always correct: molecules bearing the same functional group may have different  $\Delta_p S^\circ$  (e.g., symmetrical and unsymmetrical ketones), molecules bearing different functional groups may have identical  $\Delta_p S^\circ$  (e.g., cyanide, esters...).

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