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Proton affinities of two weakly bidentate molecules: 1,2-dimethoxyethane and methoxyacetone

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Abstract

The proton affinities (PA), of methoxyacetone and 1,2-dimethoxyethane have been determined by the kinetic method, using alkyl ethers and simple ketones having established PA values as their proton bound partners. Both compounds show effects attributed to activation entropies acting against the target molecules' retaining the proton. The PA values determined in this study were, PA methoxyacetone = 846.5 ± 2 kJ/mol; PA 1,2-dimethoxyethane = 845.5 ± 2 kJ/mol, (which is considerably lower than the previously cited value, 858 kJ/mol). The PA of cyclopentanone was revised to 828 ± 4 kJ/mol from its reference value of 824 kJ/mol. The present work showed that simple ketones and ethers, whose PA values conveniently overlap, cannot indiscriminately be used as reference compounds; care must always be taken in the choice of the proton bound partner (reference) molecule in kinetic method studies. (Int J Mass Spectrom 210/211 (2001) 147–152) © 2001 Elsevier Science B.V.

Keywords: Proton affinity; 1,2-Dimethyloxyethane; Methoxyacetone; Kinetic method

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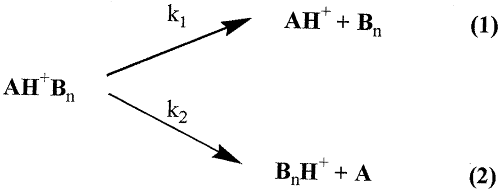
1. Introduction

The "kinetic method" has long been used for determining the proton affinity (PA) values for a very wide range of organic compounds and so has been extensively reviewed [1] and discussed [2,3].

Recent work from this laboratory [3] has aimed at clarifying the underlying physicochemical assumptions of the method and the significance of the observations, as well as providing new PA data for alkanols [3], nitriles [4], and amines [5,6].

The method involves the measurement of the relative peak heights for the fragment ions AH^+ and B_nH^+, produced by the dissociation of mass selected AH^+B_n ions. A is a molecule of unknown PA and B_n are a series of bases, preferably chemically closely similar to A, having known PA values. The ratio of the peak heights, R, in the metastable ion (MI) and collision induced dissociation (CID) mass spectra of AH^+B_n ions is assumed to be equal to the rate constant ratio, k_1/k_2 for the reactions in Scheme 1.

Expressed in terms of transition state theory:



Scheme 1

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A contribution to celebrate the retirement of a highly respected colleague, Professor N. M. M. Nibbering.

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$$\ln(k_1/k_2) = \ln Q_1^{\#}/Q_2^{\#} - (E_1^0 - E_2^0)/RT$$

where $Q_1^{\#}$ and $Q_2^{\#}$ are the partition functions for the transition states, E_1^0 and E_2^0 are the activation energies. T is (normally) the temperature in Kelvin, but for these experiments is certainly related to the internal energy of the ion, but is not yet clearly defined [3,7]. In the kinetic method k_1 and k_2 are replaced by the product ion peak intensities, $[AH^+]$ and $[B_nH^+]$, and the above equation is simplified by replacing $(E_1^0 - E_2^0)$ with the difference in PA values, $[PA(A)-PA(B_n)]$.

Our recent work [6] has led to the following conclusions concerning the validity of this simple treatment of the experimental results.

In the absence of any net entropy of activation (i.e. $Q_1^{\#} = Q_2^{\#}$), a reasonable situation for homologous species, then plots of $\ln R$ versus $PA(B_n)$ will give straight lines which intersect at $\ln R = 0$, at the PA value for A. If the lines intersect below the $\ln R = 0$ axis, then there is an entropy of activation acting against the formation of AH^+, i.e. the transition state leading to $AH^+ + B_n$ is tighter than that leading to A + B_nH^+. The general effects resulting from activation entropies have been described in terms of the relative curvatures of the $\ln k$ versus internal energy ($E^{\#}$) plots for the competing fragmentations [6]. A prominent feature arising from an entropy effect is that the R value may change from greater than 1 to less than unity when going from metastable ion (low internal energy) to CID (high internal energy) ions. In other words, the $\ln k$ versus $E^{\#}$ curves cross each other, instead of remaining essentially parallel throughout all internal energies.

A reverse energy barrier (E_{rev}) to either or both dissociation channels is not detectable by the kinetic method, even where it is known to exist from other data. For example, the bidentate species 1,3-diaminopropane and 1,4-diaminobutane both have a significant E_{rev} for their retaining the proton, and so their PA values from the kinetic method are observed to be too low [6,8].

With regard to the measurement of R, it has been found that for high-energy CID experiments (kilovolt ions), the R values are collision gas independent [3–6,9]. It is essential to apply a voltage to the collision cell in order to separate collision induced from metastable ion dissociations [3,6].

Recent experiments with 1,2-diaminoethane [6,8], showed that this molecule is only weakly bidentate, displaying a significant activation entropy effect when proton bound to simple alkylamines, but having little or no E_{rev} for its generation from AH^+B_n ions. In this short study we have investigated the PA of two other similar bidentate molecules, 1,2-dimethoxyethane and methoxyacetone, again to look for entropy and E_{rev} effects.

2. Experimental

The proton bound dimers were generated under chemical ionization conditions in the ion source of a modified triple sector VG ZAB 2F instrument of BEE geometry [10].

The compounds were admitted to the ion source with methanol to aid protonation. The AH^+ and B_nH^+ peak heights in the metastable ion and collision induced dissociation mass spectra were recorded in the second field-free region of the instrument. A potential of +500 V was applied to the collision cell to separate MI and CID signals, shifting the latter to higher translational energies. The relative abundances in the CID mass spectra were corrected for minor contributions from metastable ions [3]. The ion source temperature was maintained at ~460 K.

All compounds were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification.

3. Results and discussion

Methoxyacetone and 1,2-dimethoxyethane were proton bound to series of selected substrate bases with known PA values [11], and within a range of ~25 kJ/mol. Secondary fragmentations were minimal for all compounds investigated.

Table 1
[BH^+]/[$CH_3C(OH^+)CH_2OCH_3$] ratios in the metastable ion (MI) and collision induced dissociations (CID) of proton-bound dimers

	MI		CID		
Ketones	*R*	*ln R*	R^b	*ln R*	PA^a (kJ mol^{-1})
$CH_3COC_2H_5$	1224^c	7.1	2.7	1.0	827.3
Cyclopentanone	1097^d	7.0	2.6	0.96	823.7, $(828)^e$
$CH_3COC_3H_7$	119.0	4.8	1.6	0.5	832.7
$CH_3CO(i\text{-}C_3H_7)$	26.9	3.3	1.3	0.2	836.3
$C_2H_5COC_2H_5$	21.4	3.1	1.1	0.1	836.8
$CH_3CO(t\text{-}C_4H_9)$	2.79	1.03	0.6	−0.5	840.1
Cyclohexanone	2.88	1.06	0.5	−0.7	841.0
$C_2H_5COC_3H_7$	3.2	1.15	0.53	−0.64	843.2, $(841)^e$
$C_3H_7COC_3H_7$	0.44	−0.8	0.3	−1.2	845.0
Cycloheptanone	0.36	−1.0	0.24	−1.4	845.6
Cyclooctanone	0.05	−2.9	0.12	−2.1	849.4

[a] PA values given in NIST (1998) tables in [11].
[b] Corrected CID ratios (+500 V on the collision cell).
[c] Paired with 2-pentanone.
[d] Paired with 2-butanone.
[e] Derived from their position on the *ln R* MI and CID lines, see text for discussion.

3.1. Methoxyacetone

The ln[AH^+]/[B_nH^+] values for methoxyacetone as the unknown A, are presented in Table 1 and plotted against the reference PA data [11] in Fig. 1. The MI and CID lines were drawn in Fig. 1 with the exclusion of the ln *R* values for cyclopentanone and 3-hexanone for reasons discussed in the following.

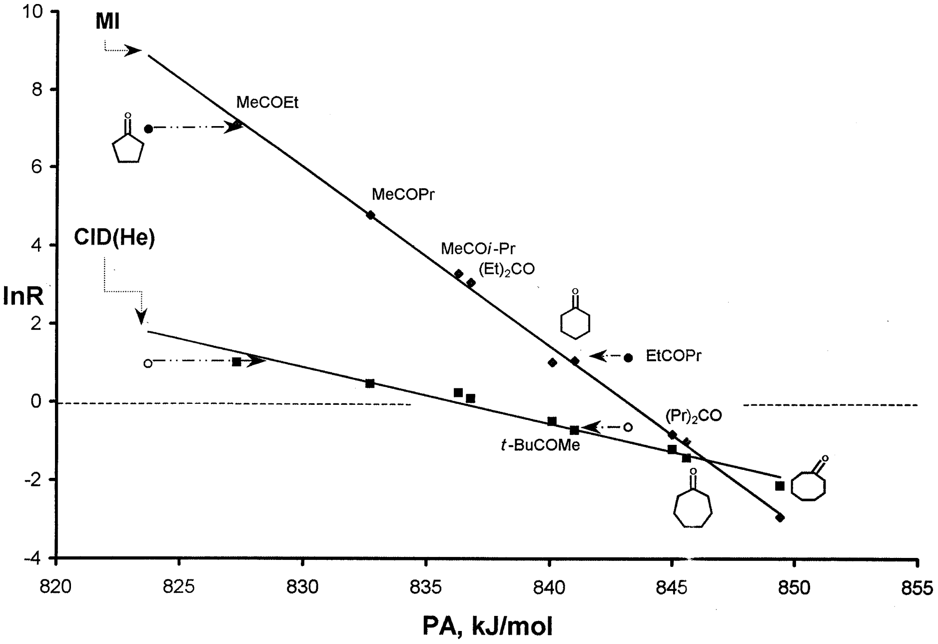

Fig. 1. Plot of ln[$(CH_3)(CH_2OCH_3)COH^+/BH^+$] vs. PA values. Arrows denote experimental values for cyclopentanone and 3-hexanone.

The intersection of the MI and CID lines gives a PA value of 846.5 kJ/mol for methoxyacetone. In the CID experiments the apparent gas phase basicity, $\Delta G^{\#}$, is lowered to 836 kJ/mol, showing the existence of a significant $T\Delta S^{\#}$ effect. For the MI experiments, involving ions having a lower internal energy, the effect is markedly less, $\Delta G^{\#}$ being 844 kJ/mol. Without an effective method for evaluating the internal energy content of the ions and relating it to a "temperature", $\Delta S^{\#}$ cannot be estimated. The $\Delta S^{\#}$ effect is also clearly apparent in the inversion of the sign of $\ln R$ from positive to negative, for cyclohexanone, 3-hexanone, and 3,3-dimethyl-2-pentanone in MI and CID experiments, respectively. The transition state leading to retention of the proton by the calibrant molecule can confidently be predicted to be looser than that where the proton is still bound to the two O atoms in the methoxyacetone, here rotational motion of the latter will be restricted.

It is noteworthy that the $\ln R$ values for cyclopentanone and 3-hexanone, relative to all the other ketones, are not very compatible with their NIST PA values, 823.7 and 843.2 kJ/mol, respectively, see Fig. 1. The PA of cyclopentanone derived from its position on the $\ln R$ MI and CID lines is ~4 kJ/mol higher than the NIST reference value [11]. However the highest GB value reported therein, 800 kJ/mol, provides a PA of ~830 kJ/mol for this molecule, in good agreement with our result, 828 kJ/mol.

To investigate this further, the R value for the cyclopentanone–2-butanone (PA 827.3 kJ/mol) proton bound dimer was measured. The result, MI, $R = 1.1$, CID $R = 1.04$, in favor of the cyclic ketone provides immediate support for the above proposal and also illustrates the considerable sensitivity of the kinetic method to small differences in PA.

The $\ln R$ values for 3-hexanone indicate that its listed PA may be slightly too high, but only by ~2 kJ/mol. This is compatible with the behavior of this ketone relative to cyclohexanone (see Table 1), where methoxyacetone provides the link. Moreover, the $\ln R$ values for the proton bound pair 3-hexanone–cyclohexanone, were MI, 1.02 and CID, 0.88. It should be noted that the ICR study by Bouchoux

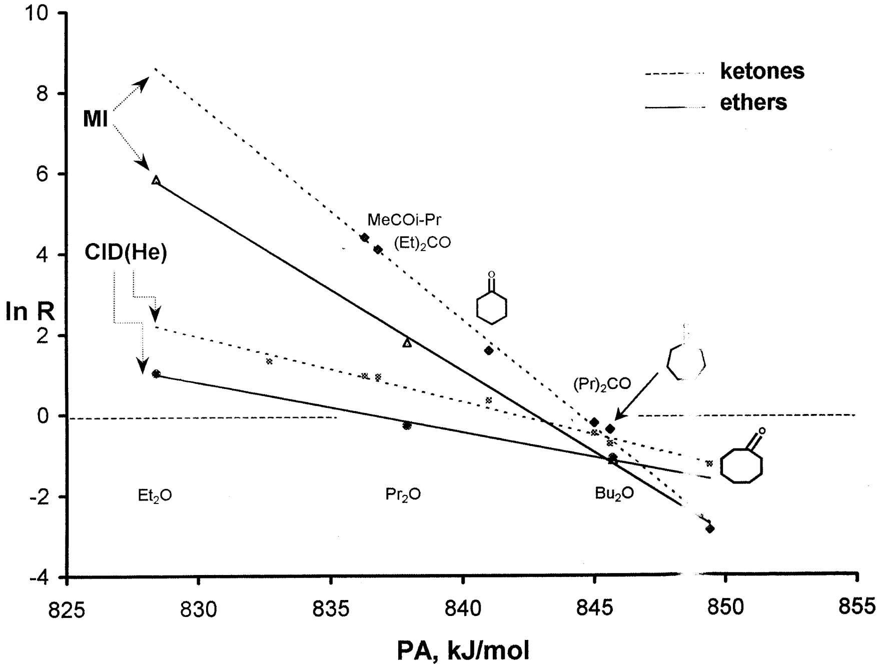

Fig. 2. Plot of $\ln[(CH_3O(CH_2)_2OH^+CH_3/BH^+]$ vs. PA values.

Table 2
$[R_2OH^+]/[CH_3O(CH_2)_2OH^+CH_3]$ ratios in the metastable ion (MI) and collision induced dissociations (CID) of proton-bound dimers

Ethers	MI		CID		PA[a] (kJ mol^{-1})
	R	ln R	R[b]	ln R	
Ethyl ether	365[c]	5.9	2.8	1.03	828.4
Propyl ether	6.1	1.8	0.79	−0.23	837.9
Butyl ether	0.32	−1.14	3.33	−1.11	845.7

[a] PA values given in NIST (1998) tables in [11].

[b] Corrected CID ratios (+500 V on the collision cell).

[c] CID value was obtained directly, whereas the MI value was recorded stepwise, that is is given by the product of the R values for $Et_2O(H)^+OPr_2$ and $Pr_2O(H)^+(CH_3OCH_2)_2$.

and Houriet [12] gave virtually identical PA values for these two ketones. Given the inherent uncertainties in reference PA data, which for equilibrium studies are typically ±2 kJ/mol [11], perhaps a correction for 3-hexanone is less well justified than that for cyclopentanone.

3.2. 1,2-Dimethoxyethane

Only three simple symmetric aliphatic ethers, $(C_2H_5)_2O$, $(C_3H_7)_2O$, and $(C_4H_9)_2O$ possess PA values close enough to the reference PA for this molecule (858 kJ/mol) to be used as standards. The $\ln[AH^+]/[B_nH^+]$ results are plotted versus these ethers' PA values in Fig. 2 and are listed in Table 2.

The crossover point of the MI and CID lines gives a PA value of 845.5 kJ/mol for dimethoxyethane. Again the lines do not cross at $\ln R = 0$, indicating the presence of an entropy ($T\Delta S\sharp$) effect of ~7 kJ/mol for CID ions, acting against the diether. The limited choice of reference ethers with well-established PA data that could be used as standards in this study, prompted us to consider other reference molecules having a different functional group, but appropriate PA values.

Because simple ketones were successfully used for the kinetic method investigation of methoxyacetone, we evaluated their compatibility with the bidentate ether, 1,2-dimethoxyethane. The results of MI and CID experiments are included in Fig. 2 and are given in Table 3. The MI and CID lines cross at the same PA value as that obtained from the experiments with the alkyl ethers, 845.5 kJ/mol.

This value is however not in agreement with the selected NIST value for 1,2-dimethoxymethane, 858.0 kJ/mol, and we argue that this is too high; the GB values in the NIST Tables are 822.8, 820.4, and 817.7 kJ/mol, which correspond to PA of 861.2, 854.0, and 847.1 kJ/mol respectively. The latter is in good agreement with the present result.

On balance, the present low value, PA $(CH_3OCH_2)_2 = 846$ kJ/mol appears to be better than the NIST selection. If the higher value (858 kJ/mol) is correct, then the discrepancy with the present result can only have arisen from a significant reverse activation energy barrier of ~13 kJ/mol. The analogous bidentate species, 1,2-diaminoethane, showed no evidence for such an E_{rev} [6]. It must however be

Table 3
$[BH^+]/[CH_3O(CH_2)_2OH^+CH_3]$ ratios in the metastable ion (MI) and collision induced dissociations (CID) of proton-bound dimers

Ketones	MI		CID		PA[a] (kJ mol^{-1})
	R	ln R	R[b]	ln R	
$CH_3COC_3H_7$			3.8	1.3	832.7
$CH_3CO(i\text{-}C_3H_7)$	81.5	4.4	2.58	0.95	836.3
$C_2H_5COC_2H_5$	60.3	4.1	2.51	0.92	836.8
Cyclohexanone	4.9	1.6	1.4	0.3	841.0
$C_3H_7COC_3H_7$	0.8	−0.2	0.6	−0.5	845.0
Cycloheptanone	0.7	−0.4	0.5	−0.7	845.6
Cyclooctanone	0.06	−2.9	0.3	−1.3	849.4

[a] PA values given in NIST (1998) tables in [11].

[b] Corrected CID ratios (+500 V on the collision cell).

emphasized that a reverse energy barrier cannot be experimentally detected by the kinetic method, but only inferred, as here, from other data, such as those derived from equilibrium studies.

Finally, note that the two standards, ethers and ketones, generate different lines in Fig. 2. Thus kinetic method experiments in which proton bound ether/ketone pairs are examined should show that for a duo with the same PA values, the ether should retain the proton. Moreover, Fig. 2 shows that for the bidentate ether, the larger entropy effect is observed with the alkyl ethers as standards. Thus a ketone/alkyl ether pair will show a entropy effect acting against the ketone. This is confirmed by the pair $(C_4H_9)_2O–H^+$-(cy-$C_7H_{14}O$), PA values 845.7 and 845.6 kJ/mol, respectively where *R* was measured to be MI $=$ 2.3 and CID $=$ 1.7, in favor of the ether. It is possible that the geometry changes leading to the disfavored transition state (nominally that in which the carbonyl group is becoming an OH substituted carbocation) introduce an entropy loss relative to the transition state with the proton established at the ether oxygen.

Such experimental results act as sharp reminders that the choice of reference compounds for kinetic method investigations should not be lightly undertaken.

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