

## Concerning the Lewis acidity of $\text{NO}^+$ and $\text{NO}_2^+$ as measured by their affinity to selected bases

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### Abstract

Recently published theoretical results concerning the  $\text{NO}^+$  and  $\text{NO}_2^+$  gas-phase affinities of a few selected molecules, as well as the correlation between the above quantities and the corresponding proton affinities, are examined in the context of the much larger body of experimental and theoretical data already reported in the literature. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Lewis acidity; Proton affinity; Acidities correlation

Recently, one of the authors (G.C.), as part of a group including Torday, Santillán, Ciuffo, Jáuregui, Pataricza, Papp and Csizmadia, has reported a theoretical study of the  $\text{NO}^+$  and  $\text{NO}_2^+$  affinities of selected bases aimed at evaluating the Lewis acidity of the cations [1]. Unfortunately, in that article no adequate reference, actually no reference at all, was given to the large body of experimental [2–17] and theoretical [4,17–26] studies published on the same subject. It appears that such an omission requires a brief comment aimed at presenting a more complete picture of the current status of the field.

In essence, in Ref. [1] the proton affinity (PA), the  $\text{NO}^+$  affinity ( $\text{NO}^+\text{A}$ ) and the  $\text{NO}_2^+$  affinity ( $\text{NO}_2^+\text{A}$ ) of six molecules, i.e.  $\text{RNH}_2$ ,  $\text{ROH}$  and  $\text{RSH}$  ( $\text{R} = \text{H}, \text{CH}_3$ ) have been computed at the HF/3-31G

and HF/6-31+G(d) levels of theory. The results computed in Ref. [1] at the higher level of theory, HF/6-31+G(d), are compared in Table 1 with those of previous experimental and theoretical studies. Let us consider first the PA values. Inspection of Table 1 shows that all the computed values reported in Ref. [1] were available in the literature, being included in the comprehensive NIST database of gas-phase PA [27]. The agreement between the results of Ref. [1] and the currently accepted experimental PA is moderate, the discrepancies ranging from ca. 4–10 kcal mol<sup>-1</sup>, which is somewhat larger than those typical of current state-of-the-art theoretical methods [28].

The situation is nearly the same as regards the computed  $\text{NO}^+\text{A}$  reported in Ref. [1]. In the first place,  $\text{NO}^+\text{A}$  scales that extend to 28 [2] and 52 [5] bases, including biologically important molecules, such as thymine [5], and a  $\text{NO}_2^+\text{A}$  scale, including 18 bases [15] are available in the literature. Even

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Table 1  
Comparison of H<sup>+</sup>, NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup> affinities (kcal mol<sup>-1</sup>)

Species	PA			NO <sup>+</sup> A			NO <sub>2</sub> <sup>+</sup> A		
	Reference [1] <sup>a</sup>	Experimental <sup>b</sup>	Theoretical <sup>c</sup>	Reference [1] <sup>a</sup>	Experimental <sup>d</sup>	Theoretical	Reference [1] <sup>a</sup>	Experimental <sup>e</sup>	Theoretical
NH <sub>3</sub>	214.47	<b>204.1</b>	204.0	26.31	<i>33.2</i>	36.3 <sup>f</sup> ,30.7 <sup>g</sup>	30.73	<b>27.2</b>	27.0 <sup>h</sup>
H <sub>2</sub> O	171.22	<b>165.1</b>	164.5	21.08	<b>18.5</b>	19.5 <sup>i</sup>	24.01	<b>19.6</b>	17.3 <sup>j</sup>
H <sub>2</sub> S	172.33	<b>168.5</b>	169.1	11.99	<i>20.1</i>		3.67	<i>20.0</i>	
CH <sub>3</sub> NH <sub>2</sub>	225.89	<b>214.9</b>	215.3	30.51	<i>37.2</i>		47.68	<i>30.7</i>	
CH <sub>3</sub> OH	188.06	<b>180.3</b>	180.3	23.26	<b>23.3</b>	25.3 <sup>k</sup>	25.18	<b>21.5</b>	19.6 <sup>l</sup>
CH <sub>3</sub> SH	190.94	<b>184.8</b>	185.6	20.24	<i>26.1</i>		18.54	23.8	

<sup>a</sup> Values computed at the HF/6-31+G (d) level of theory.

<sup>b</sup> From Ref. [27].

<sup>c</sup> From Ref. [28].

<sup>d</sup> From Ref. [5]. The data in bold characters are direct experimental measurements, those in italics from the PA/NO<sup>+</sup>A correlation.

<sup>e</sup> From Ref. [15]. The data in bold characters are direct experimental measurements, those in italics from the PA/NO<sub>2</sub><sup>+</sup>A correlation.

<sup>f</sup> From Ref. [19].

<sup>g</sup> From Ref. [20].

<sup>h</sup> From Ref. [17].

<sup>i</sup> From Ref. [4].

<sup>j</sup> From Ref. [21].

<sup>k</sup> From Ref. [18].

<sup>l</sup> From Ref. [22].

the PA/NO<sup>+</sup>A and PA/NO<sub>2</sub><sup>+</sup>A correlations of Ref. [1] that include no more than 6 bases are not unprecedented, since, analogous correlations extended to some 50 [5] and 18 bases [15], respectively, are available in the literature. With regards to the accuracy of the computed NO<sup>+</sup>A and NO<sub>2</sub><sup>+</sup>A reported in Ref. [1], inspection of Table 1 shows discrepancies from the published experimental and theoretical value that are smaller than in the case of PA, owing to the much smaller size of the quantities compared. Nevertheless, in certain cases, discrepancies do exist e.g. the NO<sub>2</sub><sup>+</sup>A of H<sub>2</sub>S, computed in Ref. [1] at the HF/6-31+G(d) level of theory, amounts to 3.67 kcal mol<sup>-1</sup>, which is lower than the NO<sub>2</sub><sup>+</sup>A of N<sub>2</sub> and CO<sub>2</sub>, computed to be 4.7 and 7.9 kcal mol<sup>-1</sup>, respectively, at higher levels of theory [25]. In view of the much higher PA of H<sub>2</sub>S than of N<sub>2</sub> and CO<sub>2</sub>, such a result can hardly fit PA/NO<sub>2</sub><sup>+</sup>A correlations, and contrasts with the much higher value, ca. 20 kcal mol<sup>-1</sup>, estimated from the available experimental PA/NO<sub>2</sub><sup>+</sup>A correlation [15].

In summary, from a survey of the pertinent literature it seems fair to conclude that the current status of the problem related to the Lewis acidity of NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup> is far more advanced than outlined in Ref. [1]. Furthermore, it appears that accurate theoretical evaluation of PA, NO<sup>+</sup>A and NO<sub>2</sub><sup>+</sup>A calls for higher level methods than those currently available and that are conveniently applicable to relatively simple species, as those reported in Ref. [1].

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