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Short communication

A mathematic model for proton affinity of organic molecules: Effect of size, chain length and nature of surrounding groups on the proton affinity of a site

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ABSTRACT

A mathematic model is proposed for proton affinity (PA) of organic molecules which accounts for the effects of size and nature of the functional groups and their distances from the proton acceptor atom. The general form of the proposed equation is $PA(n) = A + \sum_i B_i n_i + \sum_{j \geq i} (B_j - B_i) n_{j-i} - \bar{C} n^2$, where Bn and $\bar{C}n^2$ show effect of nature and size of functional groups, respectively. A, B and C are constants and n is the number of groups directly connected to the proton acceptor site. The B_j–B_i term accounts for the effect of branched alkyl chains.

1. Introduction

Proton transfer is a very important reaction which occurs in many atmospheric and biological systems [1,2]. Therefore, considerable efforts have been made for understanding the nature of this reaction and study kinetics, mechanism and thermodynamics of proton transfers in different environments [3]. Proton affinity (PA), which is the negative enthalpy ($-\Delta H$) of protonation of a molecule in gas phase, is key parameter that determines whether the proton transfer reaction occurs or not. Hence, measurement and calculation of proton affinities of different molecules using experimental techniques and theoretical methods are of interest [4–6]. Usually, in a molecule, proton affinity of nitrogen atom is more than that of oxygen atom [7], however, structure and functional groups of the molecule can influence this trend. In this work, a mathematical model is proposed which accounts for the effects of electron withdrawing/donor groups, their size and distance from the proton acceptor site, on the proton affinity of the molecule.

2. Computational details and data

Most of the proton affinities used in this work are from National Institute of Standard and Technology (NIST) website [8]. The proton affinities of $CH_2FN(CH_3)_2$, $(CH_2F)_2N(CH_3)$ and $(CH_2F)_3N$ were calculated by G4MP2 method using Gaussian 09 software [9].

3. Results and discussion

Fig. 1 shows the variations in the proton affinities of (a) H_2O, (b) CH_2O, (c) PH_3 and (d) NH_3 when their H atoms are replaced with CH_3 groups. Also, Fig. S, in Supplementary Information shows effect of addition of (a) $-CH_2OH$ and (b) phenyl groups on the proton affinity of NH_3. The experimental values are shown as points while the solid lines are fitting results. The CH_3 groups are electron donor and increase the proton affinity values, however, this increase is not linear because of steric hindrance of the CH_3 groups. An equation was proposed for proton affinity (PA) to account for effects of electron donor groups and steric hindrance as a function of the number of CH_3 groups (n)

$$PA(n) = A + Bn - Cn^2 \quad (1)$$

where A is the proton affinity of the simplest molecule (H_2O, CH_2O, NH_3 or PH_3), B is a measure of nature of the groups (CH_3, here) directly connected to the proton acceptor atom. B is positive for electron donors and negative for electron withdrawing groups. The value of B for CH_3 is about 50–72 kJ/mol. In the case of aldehydes and ketones, since the CH_3 is not directly connected to the oxygen atom, B is small. C is a measure of the size of the groups directly connected to the proton acceptor atom or the cross section of the groups and the proton acceptor site. The experimental data were

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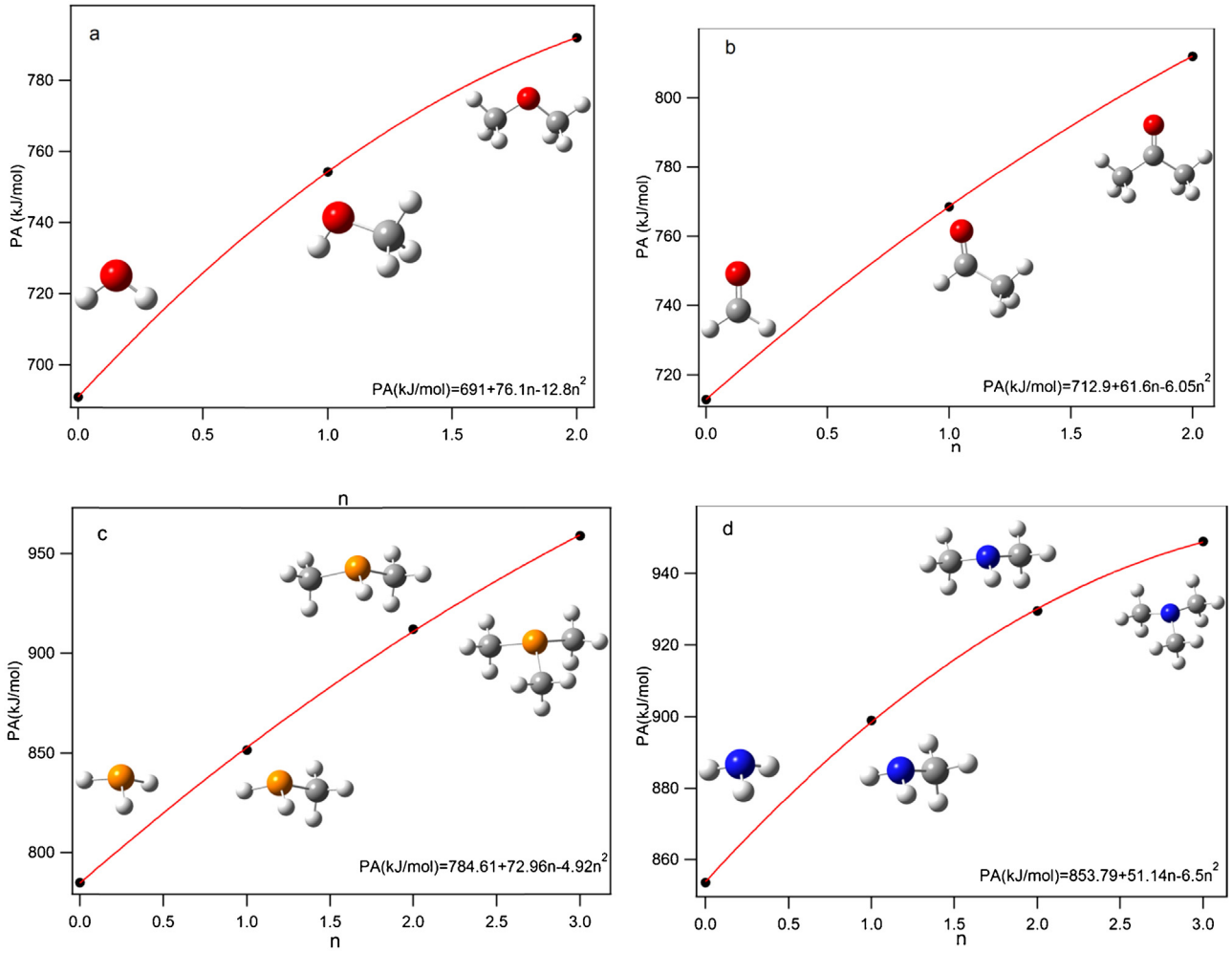

Fig. 1. The proton affinities of (a) H_2O, (b) CH_2O, (c) PH_3 and (d) NH_3 when their H atoms are replaced with CH_3 groups.

exactly fitted in the proposed equation. The steric hindrance affects the PA values with a square function of n which shows effect of cross section.

Supplementary Fig. S related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijms.2015.12.002.

Fig. 2 shows the proton affinities of linear (a) aldehydes and (b) amines. Here, the number of CH_3 groups directly connected to the acceptor atom is constant while the alkyl chain varies. Therefore, steric hindrance (Cn^2) is negligible and the distance of the $CH_{2,3}$ groups from the acceptor atom is determinant factor. As the distance of the group increases its effect on the PA decreases as an exponential function of distance (m)

$$PA(m) = A + B'm \cdot \exp[-D(m-1)] \quad (2)$$

The role of B' and B is the same and both stand for the nature of the groups. n and m may be confusing parameters. n is the number of groups directly connected to the acceptor atom ($n = 1$ in Fig. 2) while m is the length of the alkyl chain (m is variable in Fig. 2). For the CH_2 group directly connected to the acceptor atom $m = 1$;

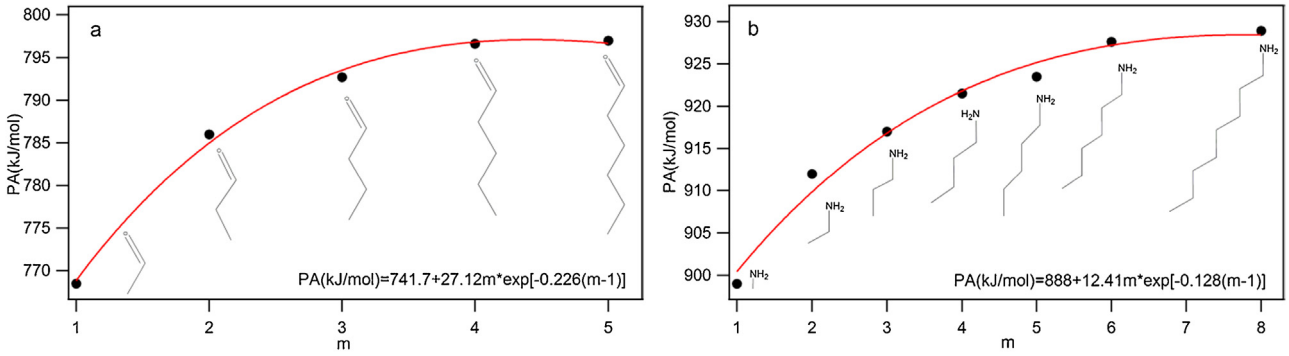

Fig. 2. The proton affinities of linear (a) aldehydes and (b) amines as a function of alkyl chain length.