ADDITIONS AND CORRECTIONS

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Paula Jaramillo, Kaline Coutinho, and Sylvio Canuto*: Solvent Effects in Chemical Processes. Water-Assisted Proton Transfer Reaction of Pterin in Aqueous Environment

Russell M. Pitzer Festschrift (DOI: 10.1021/jp903638n). In an article in this issue[1] we have considered the tautomeric reaction (A−B) of pterin shown below (Figure 1) using two

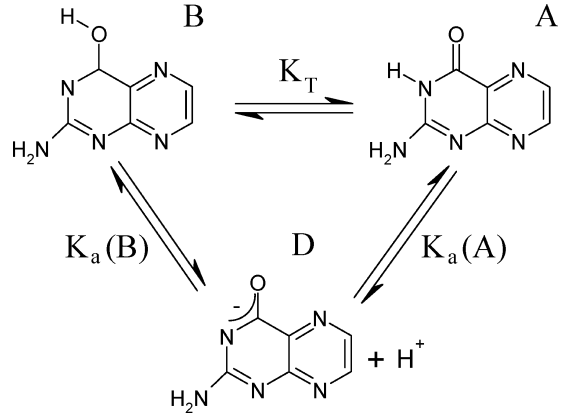

Figure 1

possible reaction paths. One involving a direct proton transfer and the other assisted by a solvent water molecule. Using these two processes in thermodynamic perturbation theory, we obtained the free energy $\Delta G_{B\rightarrow A}$. From the calculated free energies we obtained the tautomeric constant K_T for the two paths using $\Delta G_{B\rightarrow A}(\text{solv}) = -RT \ln(K_T)$. Then one can immediately obtain $pK_T = \log (K_T)$.

The theoretical determination of acid-basis pK_a has seen increasing interest in recent years and some conceptual aspects have been under intense discussion,[2−5] and a stronger conceptual basis for theoretical calculations is emerging. Although the tautomeric constant can be related to the acidity constant (Figure 1) $pK_T = pK_a(A) - pK_a(B)$, in our publication[1] we have used our calculated pK_T as a numerical value for the acid-basis $pK_a(A)$ value. This is a good approximation in the assumption that $pK_a(B)$ is very small, which seems reasonable but cannot be assured in general. Thus our reported value should be taken as a pK_T constant. More work in this direction is now in progress.

References and Notes

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