

ADDITIONS AND CORRECTIONS

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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 issue¹ we have considered the tautomeric reaction (A–B) of pterin shown below (Figure 1) using two

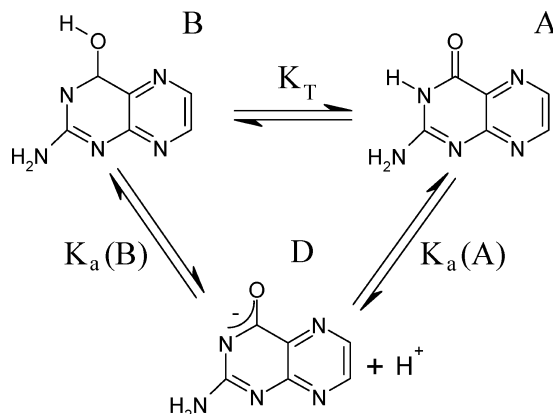


Figure 1

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 $\text{p}K_T = \log(K_T)$.

The theoretical determination of acid-basis $\text{p}K_a$ 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) $\text{p}K_T = \text{p}K_a(A) - \text{p}K_a(B)$, in our publication¹ we have used our calculated $\text{p}K_T$ as a numerical value for the acid-basis $\text{p}K_a(A)$ value. This is a good approximation in the assumption that $\text{p}K_a(B)$ is very small, which seems reasonable but cannot be assured in general. Thus our reported value should be taken as a $\text{p}K_T$ constant. More work in this direction is now in progress.

References and Notes

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