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Correct Interpretation of How Tunneling Proceeds at Low Temperatures in the Proton Transfer Reactions Involving Thiotropolone: A Comment

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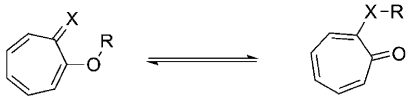
In their recent Communication,[1] Jose and Datta have performed canonical variational transition-state theory calculations with small-curvature tunneling corrections for tunneling (CVT/SCT)[2] to describe the intramolecular proton transfer processes in thiotropolone and tropolone (Reaction (1) of tautomers **1a**/**1b** and Reaction (3) of tautomers **3a**/**3b**; see Scheme 1 taken form the original Communication by Jose and Datta). These authors conclude that at temperatures below $T = 240$ K proton transfer is faster in thiotropolone than in tropolone, and that for the former molecule tunneling represents about 99% of the total process even at room temperature. The present Corrrespondence shows that their CVT/SCT calculations are incorrect, and that the conclusions derived from those calculations are erroneous and easily refuted by basic arguments of how tunneling proceeds in a chemical reaction. The Correspondence also provides the correct interpretation of tunneling effects in Reactions (1) and (3). The same arguments are also valid for the deuterium transfer in the two compounds (see Scheme 1), and therefore they are not discussed here. Details about the CVT/SCT calculations are given in the Supporting Information.



1a) X=S, R=H
2a) X=S, R=D
3a) X=O, R=H
4a) X=O, R=D

1b) X=S, R=H
2b) X=S, R=D
3b) X=O, R=H
4b) X=O, R=D

Scheme 1. Proton transfer reactions in thiotropolone and tropolone and their derivatives as given in the original Communication[1] by Jose and Datta.

In the SCT approximation quantum effects are calculated over the vibrational adiabatic potential. The profile of this potential is that of the free-energy at $T = 0$ K. At this temperature the MPW1K/6-31 + G(d,p)[3] calculations yield activation free-energies for thiotropolone and tropolone of 5.4 and 3.5 kcal mol^{-1}, respectively, as shown in Figure 1, and those values remain almost unchanged with temperature.

The calculated free-energy of activation of Reaction (1) is compatible with the value obtained from NMR experiments of Machiguchi et al.,[4] who estimated that 6 kcal mol^{-1} is the high limit for the free-energy of activation at $T = 143$ K (solid state) and at $T = 333$ K (molten state). These authors also indicated that Reaction (1) is very fast and with very little temperature dependence. However, Machiguchi et al. also noticed that the initial and final tautomeric species in thiotropolone are in the ratio of 58:42 with no temperature dependence. This ratio leads to a free-energy of reaction of about 0.1 kcal mol^{-1} (almost a thermoneutral reaction). This result is not reproduced by the MPW1K calculations, which yield a practically temperature-independent free-energy of reaction of about 3.1 kcal mol^{-1} (the percentage of the reactant tautomer in thiotropolone is close to 100% even at $T = 333$ K). The relative stability of the two wells has important consequences for the way the reaction proceeds at low temperatures, an issue I discuss below.

Reaction (3) is thermoneutral and tropolone is one of the typical examples for which the role played by quantum mechanical effects in the proton transfer process at low

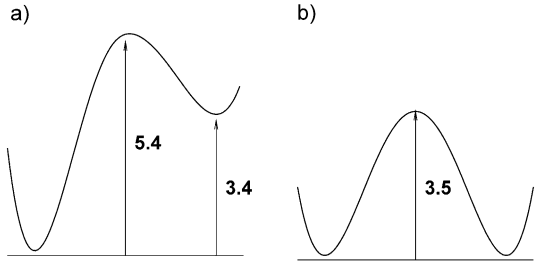


Figure 1. Free-energies of activation (in kcal mol^{-1}) for a) Reaction (1) and b) Reaction (3) at $T = 0$ K.

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temperatures is well-known. There is experimental evidence that this system exhibits splitting of the ground-state vibrational level. This is common for molecules with a symmetric double-well potential for which the wave function of the vibrational ground state is delocalized between the two wells. The wave function can penetrate in classically forbidden regions of the potential (tunneling effect) appearing at the products well. This resonance between the two wells caused by tunneling leads to splitting in the vibrational ground state. For tropolone, the ground-state tunneling splitting is $\Delta_0 = 0.97\ cm^{-1}$.[5] At the limiting case of $T = 0$ K, the thermal rate constant, k_0, has a value which is proportional to the square of Δ_0.[6] For tropolone, the low-temperature limit CVT/SCT thermal rate constant[7] predicts a value of $4.90 \times 10^9\ s^{-1}$.[8]

In this context, as shown in Figure 2, the Arrhenius plot of Reaction (3) consists of a low-temperature plateau at which most of the molecules undergo proton transfer from the zero-

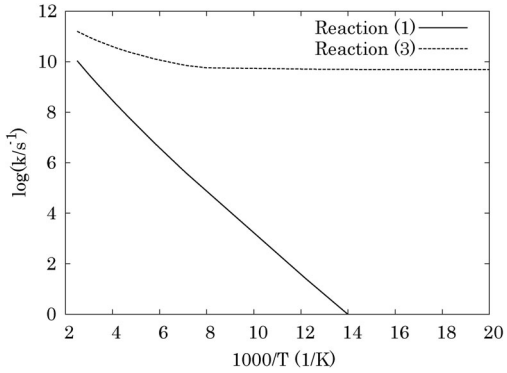

Figure 2. Arrhenius plots of the CVT/SCT thermal rate constants for Reactions (1) and (3).

point energy level. At these temperatures the process is completely dominated by tunneling.[9] As the temperature increases, higher energy levels start to have substantial population, the regime of thermally activated tunneling is reached, and the Arrhenius plot curves. If temperature raises even more, both classical over-the-barrier and non-classical reflection start to take over. At high enough temperatures the classical transfer completely dominates and the Arrhenius plot straightens.

In contrast with this picture, the MPW1K calculations predict that Reaction (1) is quite endoergic, which is incompatible with a low-temperature plateau. The reason is that at very low temperatures the molecules do not have enough energy to reach a level from which to tunnel to products and, certainly, tunneling cannot proceed from the lowest vibrational level of reactants, as claimed by Jose and Datta. Reaction (1) is different from the reactions described by Schreiner and co-workers[10] and by Zuev et al.,[11] since all those processes are exoergic and the molecules can tunnel from the ground-state vibrational level showing a low-temperature plateau. However, for Reaction (1) the calculated thermal rate constants go to zero as temperature decreases (Figure 1), and therefore Reaction (1) cannot be faster than Reaction (3). In fact, as expected, Reaction (3) is always faster than Reaction (1) in the range of temperatures from 0 to 333 K, and the Arrhenius plot of Reaction (1) shows a pronounced temperature dependence, even at low temperatures. Thus, the correctly calculated CVT/SCT activation energies for Reaction (1) at 143 and 333 K are 4.0 and 4.9 kcal mol^{-1}, respectively, and the thermal rate constants are 5.12×10^5 and $3.07 \times 10^9\ s^{-1}$, respectively. In any case these values show that the MPW1K level cannot mimic the experimental conditions.

The calculations do not support either the title claim that tunneling governs intramolecular proton transfer at room temperature in Reaction (1). The SCT transmission coefficient is 2.67 at $T = 298$ K and includes contributions of both tunneling (1.96) and non-classical reflection (0.71). Therefore, for Reaction (1) tunneling contributes about 50% to the total forward flux to products. For Reaction (3), however, tunneling does dominate the proton transfer process, its contribution at room temperature being 82%.

In summary, the MPW1K electronic structure calculations fail to reproduce the relative stability of the two tautomers in Reaction (1), under which conditions the thermal rate constant goes to zero as temperature decreases. At the same time the Arrhenius plot calculated by CVT/SCT shows a strong temperature dependence which is at odds with the experimental interpretation. The calculations also show that Reaction (3) is faster than Reaction (1) at least till $T = 333$ K, and that the latter reaction is not dominated by tunneling at room temperature.

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