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Pronounced Tunneling Effect of Proton Transfer in Thiotropolone at Room Temperature: A Reply

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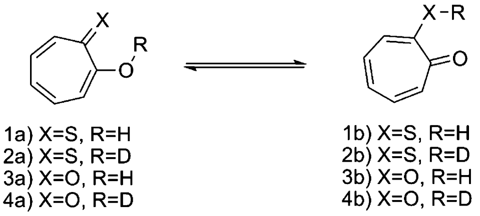
In a recent comment on our Communication,[1] Antonio Fernandez-Ramos[2] has criticized our work suggesting that tunneling effects are not important on thiotropolone (**1** in our original Communication; see Scheme 1). His argument being basically that since the process of proton transfer process from the thione (**1a**) to the enethiol (**1b**) is endoergic, at low temperatures, the molecules just do not have enough energy to tunnel from one valley to another valley. This is certainly true at very low (*T* of about 0 K) temperatures. However, even at cryogenic temperatures and certainly at room temperature, few molecules will be vibrationally excited to be able to cross to other valleys through tunneling. We agree that the potential-energy surfaces are different for thiotropolone (**1**) and tropolone (**3**). Therefore, we would like to point out that there is no disagreement with the pronounced tunneling effect of proton transfer in tropolone (**3**) and in both articles similar results are found. We also agree that the conventional way of calculating the transmission coefficient (as an integral) is not appropriate (footnote of Table S3 in the Supporting Information in Antonio Fernandez-Ramos's article) for endoergic reactions. Therefore, the formula being suggested by Fernandez-Ramos should be used instead.



Scheme 1. Proton transfer reactions in thiotropolone and tropolone and their derivatives as given in our original Communication.[1]

We would like to discuss two more aspects:

1) Based on the modified formula for the endoergic reaction of **1**, Fernandez-Ramos finds "for Reaction (1) tunneling contributes about 50% to the total forward flux to products". One should remember that this is for room temperature and we would believe that if 50% of the reaction occurs for thiotropolone at room temperature, the role of tunneling cannot and should not be underestimated. The title of our article[1] stresses the role of tunneling in thiotropolone at room temperature. Hence, we think that in light of the new calculations by Fernandez-Ramos, our statement about tunneling thiotropolone at room temperature is still valid. In fact, we believe that endoergic reactions are interesting examples where signatures of room-temperature tunneling can be easily found since, at low temperatures as correctly pointed by Fernandez-Ramos, there is hardly any reaction by either classical over the barrier process or through quantum mechanical tunneling (QMT).
2) The experimental results by Machiguchi et al.[2] indeed found very little temperature dependence for proton transfer across a broad temperature span of 190 K. Tunneling can be a plausible reason for this process. Since our calculations as well as the one by Fernandez-Ramos do not consider intermolecular effects, the role of nearest and next nearest molecules in providing vibrational assistance in tunneling cannot be ignored. A more detailed calculation at least within a quantum mechanics/molecular mechanics framework can provide a more rational explanation for the experimental phenomenon. Also, the possibility of diffusion of the proton from one molecule to another molecule through an intermolecular H bond needs to be considered. Until such a calculation is performed, the role of QMT for thiotropolone cannot be out-rightly rejected.

We believe that Fernandez-Ramos has made an important point for tunneling calculations for endoergic reactions. Quantum mechanical calculations can provide insight into the role of tunneling in many reactions. This Correspondence indeed opens up the possibility of (re)investigating many processes in chemistry and biochemistry like proton transfer in the ground and excited states where tunneling is likely to be important irrespective of their endoergic or exoergic nature.

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