Correction to Tunneling and Conformational Flexibility Play Critical Roles in the Isomerization Mechanism of Vitamin D

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Ⓢ *Supporting Information*

Page 348, last paragraph. The direct association between our eq 1 and the generalized Winstein−Holness equation of ref 42 is not correct. This entire paragraph starting with "The total isomerization ..." should read: The total isomerization rate constant should take into account all reaction paths and can be considered a multipath (MP) rate constant. The rate constants of interconversion between conformers are much faster than the individual isomerization rate constants, so the MP rate constant using approximation Y (where Y = TST or CVT/SCT) can be written as a sum of each of the individual reaction paths:

$$k^{MP,Y}(T) = \sum_{i=1}^{n_R} k_i^{W,Y}(T)$$

(1)

where n_R is the number of transition states (for Y = TST) or, equivalently, the number of reaction paths (for Y = CVT/SCT), and $k_i^{W,Y}(T)$ are the individual thermal rate constants. The superscript W indicates that the thermal rate constant is "weighted" by the whole phase space of reactants (all the conformers), because of the assumption that interconversion between conformers is faster than the isomerization reaction. It is useful to relate eq 1 with the generalized version[42] of the Winstein−Holness equation,[43] which also assumes faster interconversion between reactants. The connection between both equations is presented in the revised Supporting Information.

The Results and Discussion and the Conclusion Sections are unaffected by these changes.

Page 353. In the first sentence of the Supporting Information description, the word "equivalence" should be replaced by the word "relation".

Revised Supporting Information in which subsection S.1 entitled "Generalized Winstein−Holness equation" is replaced by "Relation between the multipath and the generalized Winstein−Holness equations".

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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