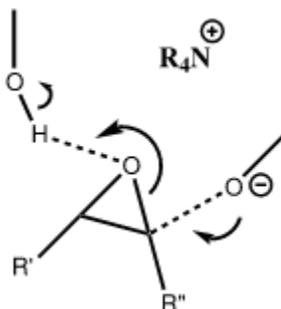


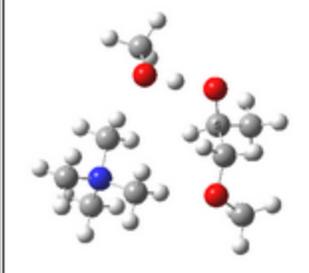
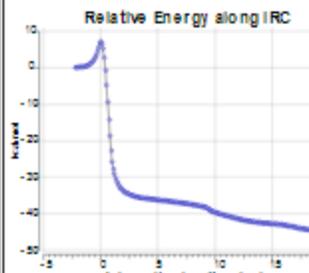
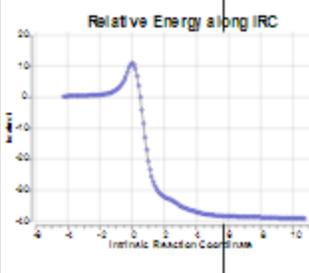
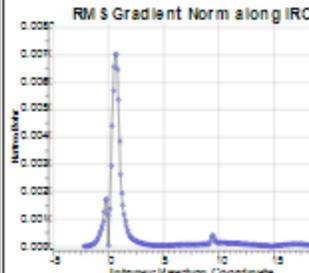
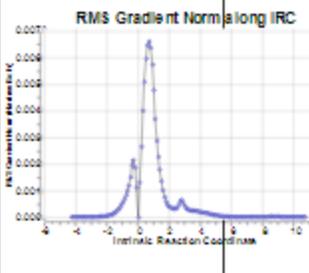
Transition states for the (base) catalysed ring opening of propene epoxide

The [previous post](#) described how the acid catalysed ring opening of propene epoxide by an alcohol (methanol) is preceded by pre-protonation of the epoxide oxygen to form a "hidden intermediate" on the concerted intrinsic reaction pathway to ring opening. Here I take a look at the mechanism where a strong base is present, modelled by tetramethyl ammonium methoxide ($R_4N^+ \cdot OMe^-$), for the two isomers $R=Me$; $R'=Me$, $R''=H$ and $R'=H$, $R''=Me$.



As noted before^[1], with alkoxide the dominant product is $R'=Me$, $R''=H$. A $\omega B97XD/6-311G(d,p)/SCRF=$ methanol) calculation of $\Delta\Delta G_{298}^\ddagger$ for the transition state for the process indeed favours this outcome, by 1.3 kcal/mol.^{[2],[3]} This corresponds to $\sim 90:10$ for $R'=Me$, $R''=H/R'=H$, $R''=Me$. The barrier in this case is significantly smaller (~ 8 kcal/mol) than was observed for the route catalysed by trifluoroacetic acid (~ 13 kcal/mol). From this emerges a possible explanation for the odd result I noted in the previous post; namely that the transition state $\Delta\Delta G^\ddagger$ for the pure water catalysed reaction was 1.7 kcal/mol *lower* for the formation of 2-alkoxy-1-propanol than for 1-alkoxy-2-propanol (*i.e.* of $R'=H$, $R''=Me$ vs $R'=Me$, $R''=H$), whereas experiment showed the dominant product was the latter. But the pure water bimolecular rate contains contributions not only from water acting as catalyst but also from the background $[H^+]$ and $[HO^-]$ rates as well (pKa methanol ~ 15.5 , pKa water ~ 15.7). Of these three bimolecular rates, it is clear that the fastest is going to be the HO^- catalysed one, and so it seems likely that the experimental result in pure water actually arises from catalysis by the $[HO^-]$ term and not by $[H_2O]$ itself.

The next task is to show how realistic the conventional "arrow pushing" for the reaction (shown above) actually is. Remember how, with acid catalysis, an IRC showed a proton transfer **preceding** the transition state. In contrast, the pure water mediated reaction showed no such pre-transfer, and instead revealed a *hidden* zwitterionic or ion-pair like intermediate occurring only **AFTER** the transition state. The MeO^- catalysed reaction is similar, except of course that with the above models ion-pairs are present both at the start and end of the reaction, with the possibility of a third **hidden ion pair** occurring somewhere along the reaction pathway. The reactant ion pair of course does have to morph into the product ion pair by virtue of a proton transfer, and this occurs **AFTER** the transition state is passed, not before.

	R'=Me, R''=H	R'=H, R''=Me
$\Delta\Delta G^\ddagger$	0.0	+1.3
IRC animation		
IRC energies		
IRC Grad		
doi:	[4]	[5]

The post-transition state proton transfer occurs driven by the need to minimise the charge separation in the ion-pair; a contact ion-pair is always likely to be more stable than a separated ion pair. For R'=H, R''=Me, a primary alkoxide is the initial product. This is relatively unstable, and so quite quickly (at about IRC 2.5) the system proceeds to acquire a proton from the adjacent methanol to reform a contact ion-pair. For R'=Me, R''=H, a secondary alkoxide is formed, which proves somewhat tardier in acquiring that proton, at IRC 9.5 in fact! Up to that point of course, the secondary alkoxide anion is a "hidden intermediate", albeit very much on the verge of becoming a proper intermediate.

This third post on the topic I think ties up some of the loose ends, and seems to cast some interesting new light on what, at face value, seems a very simple organic reaction. There is, I think, still much to learn about such "simple" reactions.

References

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