In-Class Solutions: Proton-Mediated S_N1 Mechanisms



Here, I've used Br⁻ as the base in the second step. I could also have used methanol as the base. Which is better? The conjugate acids of Br⁻ and CH₃OH (HBr and CH₃OH₂⁺) have very similar pK_a values. So we'd expect the two bases would have very similar basicities.

One incorrect mechanism that students sometimes draw is to deprotonate methanol first (with either methanol or bromide serving as the base), and then have methoxide attack as the nucleophile. There is no way that this would happen, because making a methoxide with a weak base would be pretty endothermic (kind of like making OH^- and H_3O^+ from two water molecules is), and wouldn't occur to any significant extent.



One alternative here would have been to make OH^- leave first, have it deprotonate HBr, and then follow with Br⁻ attack. But OH^- is a horrible leaving group, and it would never ever exist in strong acid like H_2SO_4/HBr . Given that, the better approach outlined here is to go back and protonate the oxygen first (to make $-OH_2^+$, a fantastic leaving group), so that OH^- doesn't have to be invoked in the first place.