

**Text Related to Segment 13.03 ©2002 Claude E. Wintner**

When ethanol is treated with concentrated hydrogen bromide, the product is bromoethane:

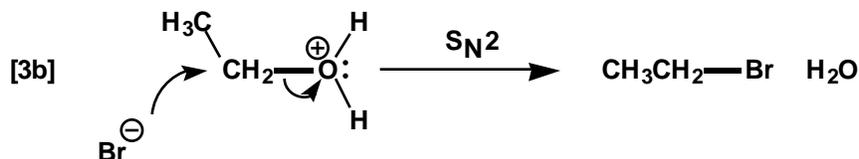
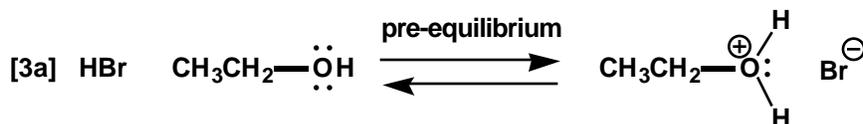
transformation:



balanced equation:



mechanism:



**ethanol and HBr yield bromoethane in a reaction governed by the S<sub>N</sub>2 mechanism**

The figure is arranged according to the rubrics previously outlined, that is, the *transformation* [1], the *balanced equation* [2]), and the *mechanism* [3a,b]. The rate law is second order, with dependence on the concentrations of both ethanol and bromide ion. However, we must *not* allow ourselves to be misled into thinking that this could be an S<sub>N</sub>2 displacement of hydroxide ion by bromide ion! First of all,

bromide ion is a far weaker base than is hydroxide ion. Secondly, hydroxide ion cannot exist in any effective concentration in a strong acid medium such as aqueous HBr; on the contrary, *the strongest base that one can invoke under these conditions is water.*

Instead, we must remember that ethanol is a Lewis base at oxygen, and that thus it can accept a proton from the strong acid HBr [3a] to form the corresponding oxonium ion. Now when bromide ion attacks the oxonium ion to form bromoethane [3b], *the departing species is the weak base water*, an acceptable leaving group under these conditions.

Despite this attractive analysis, we should not sweep under the rug a somewhat troublesome point: when HBr is dissolved in water, we know that hydronium ion and bromide ion are the products. *Water wins* the competition with bromide ion for the proton, while we are saying that it *loses* the competition with bromide ion for what amounts to a positively charged ethyl group (we soon shall discuss such a group in greater detail). In fact, we are poised just on the "thermodynamic edge" here, and there are (at least!) two related things to say about this situation. First, a high concentration of bromide ion, in other words, a concentrated HBr solution, is necessary to drive the reaction to the side of bromoethane. Secondly, and critical to the argument, the gap between the Br—H and the H—O bond energies is somewhat larger than the gap between the Br—C and the C—O bond energies. Although in *each* case the balance lies on the side of the bond to *oxygen* at standard state concentrations, in the carbon case the gap is just small enough so that the high concentration of bromide ion effectively can reverse the direction of the equilibrium. We shall run into similar circumstances in a related set of reactions.