Kinetic (Rate) Versus Thermodynamic (Equilibrium) Control of Reactions

In the reaction of 1,3-butadiene with HBr, the protonation of one of the double bonds results in the formation of a carbocation reaction intermediate. This intermediate is stabilized by resonance and the positive charge is not associated with a single carbon atom but rather with three atoms. This intermediate is shown in the figure below. Once this intermediate forms, there are two possible pathways that can lead to two different substitution products (1,2 and 1,4). Although the 1,2 product is less stable than the 1,4 product, it forms faster because of a lower E_{act} of the reaction. Although the reaction is reversible, when the 1,4 product is formed it is less likely that the reaction will go "backwards" to the intermediate because of the large E_{act} of the reverse reaction. The reverse of the 1,2 reaction is significantly easier because of the higher energy of the product. At – 80°C the reaction produces 80% 1,2 addition and only 20% 1,4 addition. At this low temperature the reverse reaction is not a factor for either product and the reaction percentages are determined by which product forms fastest (Kinetic Control). However, if the temperature is raised to + 40°C the reaction produces only 20% 1,4 product and 80% 1,2 product. This is due to the fact that sufficient energy is present to cause a reasonable rate for the reverse of the 1,2 reaction but not for the 1,4 reaction. Once formed, 1,4 product stays as 1,4 product. The 1,2 product may undergo the reverse reaction and ultimately end up as 1,4 product. In this case the stability of the products is the major determinant of the product ratios and the reaction is said to be under Equilibrium Control.