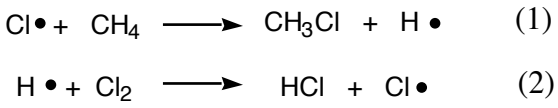
WORKSHOP 4

Alcohols and Alkyl Halides

1. The reaction of HBr with 2–methyl-2-propanol can, in principle, proceed by either an S_N1 or S_N2 mechanism. Show complete mechanisms for each of these processes, using curved arrows to indicate the movement of electron pairs. Construct reaction energy diagrams that describe the energy of the system as a function of the progress of the reaction in each case. On your diagram, clearly label the positions of the reactants, any intermediate(s), and the product. Also, specify the energy difference that corresponds to the ΔH for the overall reaction and the energy difference that corresponds to the activation energy for each step. Explain (in words) what is happening as the system makes its way from reactants to product. Indicate at what point in the mechanism the selection of a preferred mechanism occurs and how the reaction coordinate diagrams help to illustrate the preference.

Repeat this exercise with the reaction of HBr and methanol.

2. Consider the chlorination of methane. An alternative to the accepted mechanism for the propagation steps in the chlorination of methane is given below.



This mechanism does not operate to any significant extent under normal conditions. Calculate ΔH for each step and suggest a reason why this mechanism cannot compete with the accepted one.

When a small amount of iodine is added to a mixture of chlorine and methane, it prevents chlorination from occurring. Therefore, iodine is a free-radical inhibitor for this reaction. Calculate ΔH values for the possible reactions of iodine with species present in the chlorination of methane, and use these values to explain why iodine inhibits the reactions.