

Section B

Question 13

(a) An S_N1 substitution reaction is a two-step reaction. The first step involves loss of a leaving group to form a carbocation intermediate:



This first step is the slow, rate-limiting step. The faster, second step involves attack on the carbocation by a nucleophile, Nu^- (shown as Nu in Equation 4):



The reaction-coordinate diagram is shown in Figure 3. The rate equation is

$$\text{rate} = k[\text{substrate}] \quad (5)$$

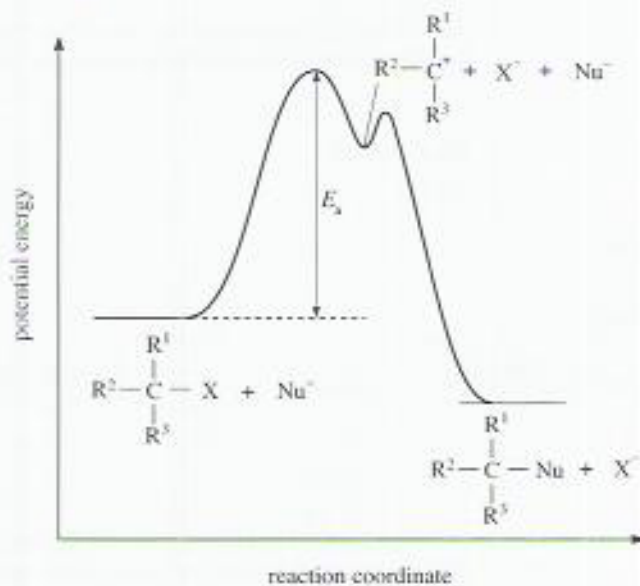
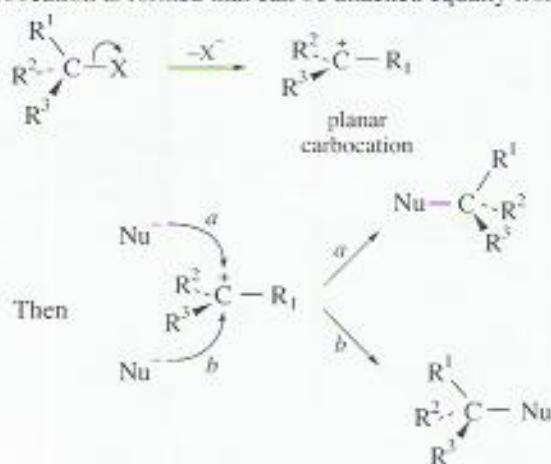


Figure 3 The reaction-coordinate diagram for an S_N1 substitution reaction.

If an optically active substrate is used, a racemic product mixture is formed. A planar carbocation is formed that can be attacked equally from either side of the plane.



SCHEME 2

- (i) Since the nucleophile is not involved in the slow, rate-limiting, first step, its nucleophilicity has no effect on the rate of the reaction.
- (ii) Since a carbocation is formed as an intermediate, the reaction goes faster for tertiary substrates, which form (most stable) tertiary carbocations. Next come secondary substrates, which form (less stable) secondary carbocations. Finally, come primary substrates, which form (even less stable) primary carbocations.