1 The order of reactivity of following alcohols with halogen acids is ..... .

(A) $CH_3CH_2—CH_2—OH$

(B) $CH_3CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}—OH$

(C) $CH_3CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—OH$

(a) (A) > (B) > (C)
(b) (C) > (B) > (A)
(c) (B) > (A) > (C)
(d) (A) > (C) > (B)

(b) Reaction between alcohols and halogen acid follows S_N1 mechanism. In S_N1 mechanism carbocations are formed as intermediates.

Let us consider the formation of carbocations with the given three alcohols.

$$CH_3—CH_2—CH_2—OH \longrightarrow CH_3—CH_2—\overset{+}{C}H + OH^-$$

In this case, 1° carbocation is formed. It is least stable. So, here S_N2 mechanism is followed. In this S_N2 mechanism a transitory state is observed in α-carbon is linked with two nucleophiles.

$$CH_3—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}—OH \longrightarrow CH_3—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle +}{\overset{|}{CH}}} + OH^-$$

2°carbocation (more stable than 1°carbocation)

$$CH_3—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—OH \longrightarrow H_3C—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C^+}}}} + OH^-$$

3°carbocation (most stable)

The reaction proceeded with stable carbocation. Higher the stability of carbocation, higher will be the possibilities of attack of X^- ion to the carbocation.

As, the tertiary carbocation is most stable so the possibilities of attack of X^- ion are more prominent in case of tertiary carbocations. Thus, attack of X^- ion to carbocation is proceeded with tertiary carbocation as follows

$$H_3C—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C^{\oplus}}}}} + X \longrightarrow H_3C—CH_2—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—X$$

3°carbocation

So, the correct option is (b).

Note *Higher the stability of intermediate, higher will be the reactivity of compound and higher will be the yield of the desired product.*