According to classical resonance theory, electron delocalization could occur only via parallel overlap of p orbitals. According to hyperconjugation, also known as no-bond resonance, and a variant of resonance theory, electron delocalization could also occur via parallel overlap of p orbitals with hybridized orbitals participating in sigma bonds. For example, consider the ethyl carbocation (1), which is shown in a specific conformation (2) below.

In 2, the empty p orbital on C₁ and the sp³-hybridized orbital on C₂ participating in C₂—H₁ bond are more or less parallel, allowing parallel overlap, which lowers the electron deficiency at C₁ but makes the H₁ electron deficient.

This overlap is not strong enough to completely prevent the free rotation around the C₁—C₂ bond. Consequently, C₂—H₂ bond and C₂—H₃ bond could also share electrons with the empty p orbital on C₁.

The structure of the ethyl carbocation, according to the theory of hyperconjugation, can be shown conveniently using a series of resonance forms.
Based on the above resonance forms, the structure of the ethyl carbocation can be shown roughly as follows.

Due to hyperconjugation, in the ethyl carbocation, the net charge of +1 is shared by a total of four atoms, one carbon atom and three hydrogen atoms. Shown below are the resonance forms of the isopropyl carbocation (2), a secondary carbocation.
Based on the resonance forms, the hybrid can be shown roughly as follows.

Due to hyperconjugation, in the isopropyl carbocation, the net charge of +1 is shared by a total of seven atoms, one carbon atom and six hydrogen atoms. Thus, the net charge of +1 is delocalized over a greater number of atoms in the isopropyl carbocation than in the ethyl carbocation. The isopropyl carbocation should, therefore, be more stable than the ethyl carbocation. This prediction is consistent with the observation that secondary alkyl carbocations are more stable.
than primary alkyl carbocations.

Contributors

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