10.8: ACIDITY OF TERMINAL ALKYNES AND ACETYLIDE IONS

Learning Objectives

- explain why alkynes are more acidic than alkanes and alkenes
- predict the products and specify the reagents to generate nucleophilic acetylide ions and heavy metal acetylides

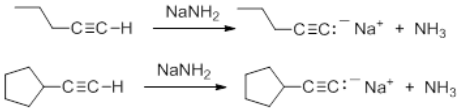
ACIDITY OF TERMINAL ALKYNES AND ACETYLILDE ION FORMATION

Terminal alkynes are much more acidic than most other hydrocarbons. Removal of the proton leads to the formation of an acetylide anion, $RC{\equiv}C{:}^{-}$. The origin of the enhanced acidity can be attributed to the stability of the acetylide anion, which has the unpaired electrons in an sp hybridized orbital. The stability results from occupying an orbital with a high degree of s-orbital character. There is a strong correlation between s-character in the orbital containing the non-bonding electrons in the anion and the acidity of hydrocarbons. The enhanced acidity with greater s-character occurs despite the fact that the homolytic C-H BDE is larger.

***Table 9.7.1**: Akynes*

Compound	Conjugate Base	Hybridization	"s Character"	pKa	C-H BDE (kJ/mol)
CH_3CH_3	$CH_3CH_2^-$	sp^3	25%	50	410
CH_2CH_2	CH_2CH^-	sp^2	33%	44	473
HCCH	HCC^-	sp	50%	25	523

Consequently, acetylide anions can be readily formed by deprotonation using a sufficiently strong base. Amide anion (NH_2^-), in the form of $NaNH_2$ is commonly used for the formation of acetylide anions.



Exercise

1. Given that the p*K*a of water is 14.00, would you expect hydroxide ion to be capable of removing a proton from each of the substances listed below? Justify your answers, briefly.
    1. ethanol (p*K*a = 16)
    2. acetic acid (p*K*a = 4.72)
    3. acetylene (p*K*a = 25)

Answer

Answers:

1.

1. No, The p*K*a of ethanol is similar to the pKa of water so proton exchange is comparable for both protonation and deprotonation between alcohols and water. Alcohols can be considered "alkylated water" and share many similarities in both physical properties and chemical reactivity.
2. Yes, very well. There is a difference of 11 p*K*a units between the p*K*a of water and the p*K*a of acetic acid. The equilibrium lies well to the right with acetate as the predominate form of the original acetic acid.
3. No, hardly at all. The hydroxide ion is too weak a base to remove a proton from acetylene. The equilibrium lies so far to the left that it is considered a "No Reaction".

CONTRIBUTORS AND ATTRIBUTIONS

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