

9.7: ALKYNE ACIDITY - FORMATION OF ACETYLIDE ANIONS

OBJECTIVES

After completing this section, you should be able to

1. write an equation for the reaction that occurs between a terminal alkyne and a strong base, such as sodamide, NaNH_2 .
2. rank a given list of compounds, including water, acetylene and ammonia, in order of increasing or decreasing acidity.
3. rank a given list of hydrocarbons, such as acetylene, ethylene and ethane, in order of increasing or decreasing acidity.
4. describe a general method for determining which of two given compounds is the stronger acid.
5. provide an acceptable explanation of why terminal alkynes are more acidic than alkanes or alkenes.

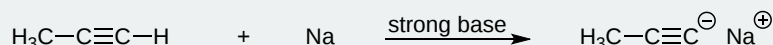
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- acetylide anion
- acidity order

STUDY NOTES

An *acetylide anion* is an anion formed by removing the proton from the end carbon of a terminal alkyne:

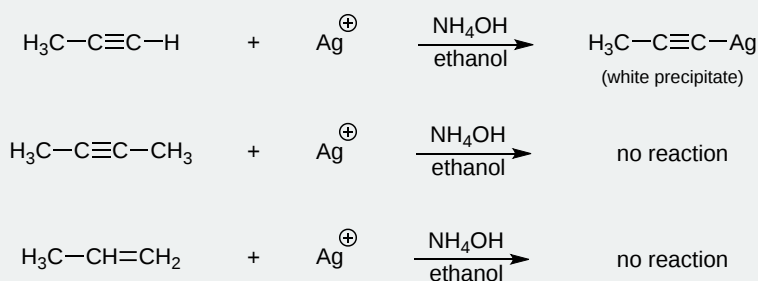


An *acidity order* is a list of compounds arranged in order of increasing or decreasing acidity.

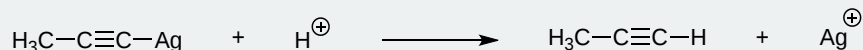
The general ideas discussed in this section should already be familiar to you from your previous exposure to chemistry and from the review in Section 2.8. A slightly different account of why terminal alkynes are stronger acids than are alkenes or alkanes is given below. However, the argument is still based on the differences between sp -, sp^2 - and sp^3 -hybrid orbitals.

The carbons of a triple bond are sp -hybridized. An sp -hybrid orbital has a 50% s character and a 50% p character, whereas an sp^2 -hybrid orbital is 33% s and 67% p , and an sp^3 -hybrid orbital is 25% s and 75% p . The greater the s character of the orbital, the closer the electrons are to the nucleus. Thus in a $\text{C}(sp)\text{-H}$ bond, the bonding electrons are closer to the carbon nucleus than they are in a $\text{C}(sp^2)\text{-H}$ bond. In other words, compared to a $\text{C}(sp^2)\text{-H}$ bond (or a $\text{C}(sp^3)\text{-H}$ bond), a $\text{C}(sp)\text{-H}$ bond is very slightly polar: $\text{C}^{\delta-}\text{-H}^{\delta+}$. This slight polarity makes it easier for a base to remove a proton from a terminal alkyne than from a less polar or non-polar alkene or alkane.

As you will appreciate, the reaction between sodium amide and a terminal alkyne is an acid-base reaction. The sodium acetylide product is, of course, a salt. Terminal alkynes can also form salts with certain heavy-metal cations, notably silver(I) and copper(I). In the laboratory component of this course, you will use the formation of an insoluble silver acetylide as a method for distinguishing terminal alkynes from alkenes and non-terminal alkynes:

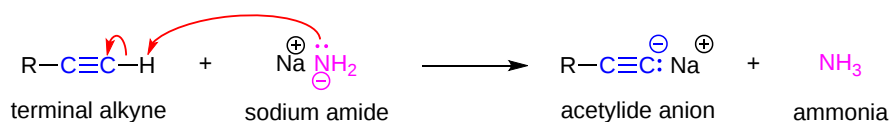


Metal acetylides are explosive when dry. They should be destroyed while still wet by warming with dilute nitric acid:

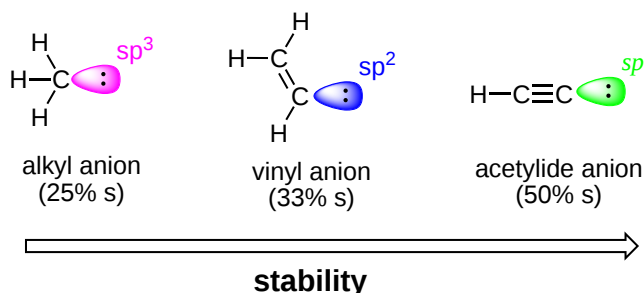


ACIDITY OF TERMINAL ALKYNES: FORMATION OF ACETYLIDE ANIONS

Terminal alkynes are much more acidic than most other hydrocarbons. Removal of the terminal proton leads to the formation of an acetylide anion, $\text{RC}\equiv\text{C}^{\ominus}$.



As discussed in [Section 2.10](#), acidity typically increases with the stability of the corresponding conjugate base. The origin of the enhanced acidity of terminal alkynes can be attributed to the stability of the acetylide anion, which has the unpaired electrons in an sp hybridized orbital. The hybridization of an orbital affects its electronegativity. Within a shell, the s orbitals occupy the region closer to the nucleus than the p orbitals. Therefore, the spherical s orbitals are more electronegative than the lobed p orbitals. The relative electronegativity of hybridized orbitals increases as the percent s character increases and follows the order $sp > sp^2 > sp^3$.



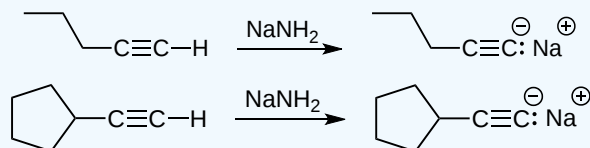
This trend indicates the sp hybridized orbitals of the acetylide anion are more electronegative and better able to stabilize a negative charge than sp^2 or sp^3 hybridized orbitals. There is a strong correlation between s -character in the orbital containing the non-bonding electrons in the anion and the acidity of hydrocarbons. The table below shows how orbital hybridization compares with the identity of the atom when predicting relative acidity. Remember that as the pK_a of a compound decreases its acidity increases.

Table 9.7.1: Alkynes

Compound	Conjugate Base	Hybridization	"s Character"	pK_a	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

Acetylene, with a pK_a of 25 is shown to be much more acidic than ethylene ($pK_a = 44$) or ethane ($pK_a = 50$). Consequently, acetylide anions can be readily formed by deprotonation of a terminal alkynes with a sufficiently strong [base](#). The amide anion (NH_2^-), in the form of sodium amide (NaNH_2) is commonly used for the formation of acetylide anions.

✓ EXAMPLE 9.7.1



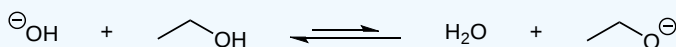
? EXERCISE 9.7.1

Given that the pK_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.

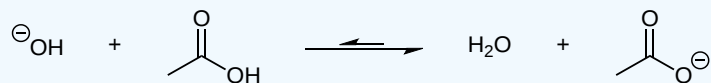
- ethanol ($pK_a = 16$)
- acetic acid ($pK_a = 4.72$)
- acetylene ($pK_a = 25$)

Answer

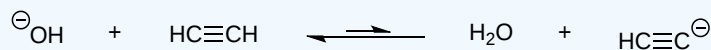
- No, not very well. The pK_a of ethanol is greater than that of water, thus the equilibrium lies to the left rather than to the right. Add texts here. Do not delete this text first.



b. Yes, very well. There is a difference of 11 pKa units between the pKa of water and the pKa of acetic acid. The equilibrium lies well to the right.



c. No, hardly at all. The hydroxide ion is too weak a base to remove a proton from acetylene. The equilibrium lies well to the left.



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