

Why the Second π -Bond Exceptionally Effective on pK_a Values of -ynoic ($-C\equiv C-$) Compounds? Chemical Education Perspective

R. Sanjeev¹, D. A. Padmavati², V. Jagannadham^{2,*}

¹Department of Chemistry, Geethanjali College of Engineering and Technology, Cheeryal-501301, Telangana, India

²Department of Chemistry, Osmania University, Hyderabad-500007, India

*Corresponding author: jagannadham1950@yahoo.com

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Abstract Sudden decrease of nearly more than two orders of magnitude of pK_a units of ynoic series of compounds is explained based on the electronegativity differences of sp, sp² and sp³ carbons and on the subsequent stability of the corresponding anions. Both resonance and inductive effects operate in tandem to stabilize the ynoic anions.

Keywords: Ynoic compounds, chemical education, graduate research; pH and pK_a

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1. Introduction

Study of acidities of carboxylic acids, alcohols, hydrocarbons, amines, and any of the compounds that have dissociable hydrogen in terms of pH and pK_a values is a common practice in an undergraduate and graduate research program. pH is nothing but the negative logarithm of hydrogen ion concentration introduced by Sørensen in 1909 [1]. pK_a is a property that is used to quantify the strength of an acid.

2. Methods

The chemical structures are drawn using chemdraw. The collection of pK_a values of the compounds are from references [2,3].

3. Discussion

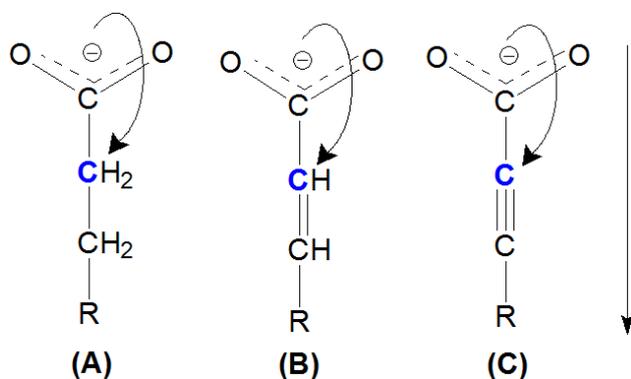
Table 1 is the summary of the pK_a and K_a data of series of oxygen, carbon and nitrogen acids and their corresponding unsaturated derivatives with a double and triple bond respectively. Looking at the pK_a values of the carboxylic acids 1-6 (Table 1) immediately comes to the mind that the first two members of these acids 1 and 2; and 4 and 5 both the series have comparable pK_a s. They differ in their acidities (ratios of K_a) by a factor of only 1.66 and 3.16 respectively. But addition of the second π -bond in the acids make them stronger by a factor of 148 and 245 times, and 230 and 725 times than their

corresponding saturated acid and the acid with a double bond respectively. This sudden increase in acidity of the acids 3 and 6 with additional π -bond is explained in terms of the different hybridizations of the carbons adjacent to the $-COOH$ group i.e., the second blue carbon (RCH_2CH_2COOH). In acids 1 and 4 those carbons are sp³ hybridized, in acids 2 and 5 they are sp² hybridized and in acids 3 and 6 they are sp hybridized. And the number of pi-electrons participating in delocalization in ynoic acids is double the number contributing extra stability of the corresponding carboxylate ion.

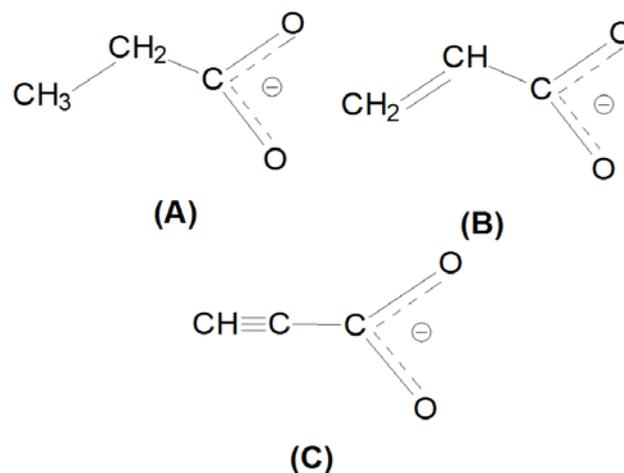
The 's' character of carbon in sp³ hybridization is 25%, in sp² hybridization it is 33.33% and sp hybridization it is 50% respectively. And it is known that the electronegativity of sp carbon > sp² carbon > sp³ carbon [4]. The more is the electronegativity of a species higher would be its capacity to attract electrons. The increase in percentage 's' character from sp³ carbon to sp² carbon is 8.33 and that of sp² carbon to sp carbon it is 16.67. It is to be observed that by addition of a second π -bond the increase in percentage 's' character is twice due to the first π -bond. This makes the sp carbon (in blue) of structure C of scheme 1 more and more electronegative. This makes the carboxylate anions of ynoic acids more and more stable. Hence the acids 3 and 6 (Table 1) are much stronger than the acids 1 and 2; and 4 and 5 respectively. Looking at the carboxylate anion structures, it will be clear that the $-COO^-$ group is more stabilized by a sp carbon because the linear structure and cylindrical geometry of the triple bond greatly helps the delocalization (scheme 2, structure C). Further both resonance and inductive effects operate in tandem to stabilize the 3-phenylpropionic acid and propionic acid carboxylate anions.

Table 1. pK_a data of the compounds

Sl. No.	acids	pK_a	K_a
1	$C_6H_5CH_2CH_2COOH$ 3-phenylpropionic acid	4.66	2.19×10^{-5}
2	$C_6H_5CH=CHCOOH$ Cinnamic acid	4.44	3.63×10^{-5}
3	$C_6H_5C\equiv CCOOH$ 3-phenylpropionic acid	2.27	5.37×10^{-3}
4	CH_3-CH_2COOH Propionic acid	4.75	1.78×10^{-5}
5	$CH_2=CHCOOH$ Acrylic acid	4.25	5.62×10^{-5}
6	$CH\equiv CCOOH$ Propiolic acid	1.89	1.29×10^{-2}
Sl. No.	alcohols	pK_a	K_a
7	1-Propanol $CH_3CH_2CH_2OH$	16.9	1.26×10^{-17}
8	Allyl alcohol $CH_2=CHCH_2OH$	15.5	3.16×10^{-16}
9	Propargyl alcohol $CH\equiv CCH_2OH$	13.6	2.51×10^{-14}
Sl. No.	hydrocarbons	pK_a	K_a
10	Propane $CH_3CH_2CH_3$	51.0	1.0×10^{-51}
11	Propene $CH_3CH=CH_2$	43.0	1.0×10^{-43}
12	Propyne $CH_3C\equiv CH$	25.0	1.0×10^{-25}
Sl. No.	amines	pK_a	K_a
13	$CH_3CH_2CH_2NH_2$ propylamine	10.84	1.45×10^{-11}
14	$CH_2=CHCH_2NH_2$ Allylamine	9.69	2.04×10^{-10}
15	$CH\equiv CCH_2NH_2$ propargylamine	7.89	1.29×10^{-8}



Scheme 1.



Scheme 2.

Same trends are observed in alcohols, hydrocarbons, and amines in their acidities (Table 1).

4. Conclusions

The second π -bond of -ynoic ($-C\equiv C-$) compounds is exceptionally effective on pK_a values.

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