

Why Cyclohexatriene (C_6H_6 , $pK_a = 43$) is Less Acidic than Cyclopentadiene (C_5H_6 , $pK_a = 15$) and Cycloheptatriene (C_7H_8 , $pK_a = 36$): A Freshmen Chemical Education Undergraduate Exercise

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Abstract The pK_a of Cyclohexatriene (Benzene) is 43. And that of Cyclopentadiene and Cycloheptatriene are 15 and 36 respectively. In the ascending order of number of carbon atoms of the three cyclic hydrocarbons, Cyclohexatriene lies between Cyclopentadiene and Cycloheptatriene. It is a tempting belief of undergraduate chemists who begin to pursue their undergraduate course that the pK_a s will be in the same increasing order with increase in ring size. But surprisingly pK_a of Cyclohexatriene is more than that of either Cyclopentadiene and or Cycloheptatriene. Suitable explanations are given.

Keywords: Cyclohexatriene, Cyclopentadiene, Cycloheptatriene and pK_a

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1. Introduction

Cyclopentadiene, Cyclohexatriene, Cycloheptatriene are three unsaturated cyclic hydrocarbons in a row. They are weak cyclic carbon acids with pK_a values of 15, 43, and 36 respectively [1,2,3]. It will be expected by the undergraduate students that as the ring size increases the pK_a s would have been in the same increasing order. But the compound which lies in between the three, cyclohexatriene has lower acidity with higher pK_a than the other two. A detailed account has been discussed.

2. Methods

The pK_a values of Cyclopentadiene, Cyclohexatriene, Cycloheptatriene are from the references [1,2,3]. Chemical structures were drawn using ChemDraw.

3. Discussion

The proton dissociation equilibriums of Cyclopentadiene, Cyclohexatriene, Cycloheptatriene are shown in Figure 1:

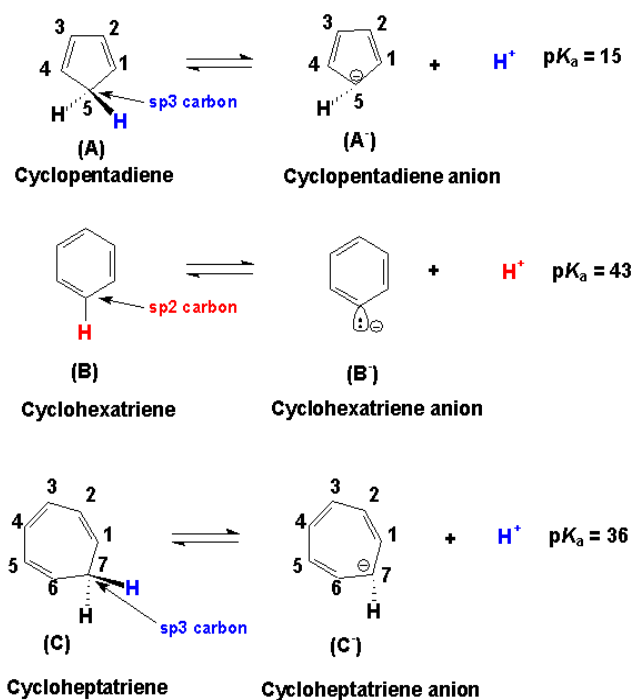


Figure 1.

Indisputably, the main difference between the three dissociation equilibriums of Cyclopentadiene, Cyclohexatriene,

Cycloheptatriene is that the deprotonation occurs in Cyclohexatriene from a sp² carbon and the deprotonation from the other two compounds are from the sp³ carbons. It is known that the sp²-hybridized carbons are slightly more electronegative than the sp³-hybridized carbons by 0.2 electronegative units [4]. Hydrogen attached to more electronegative atom is less susceptible for deprotonation makes the acid weak. Here it is noteworthy to recall the pK_as of halogen acids 3.1 (HF), -3.9 (HCl), -5.8 (HBr), -10.4 (HI) [5]. The acid with hydrogen attached to more electronegative fluorine is HF least acidic with highest pK_a and HI is most acidic with least pK_a with hydrogen attached to least electronegative iodine. Therefore, Cyclohexatriene having dissociable hydrogen attached to more electronegative sp²-carbon will be less acidic than the rest of the two enes with hydrogens attached to less electronegative sp³-carbons.

Another important factor to explain the pK_a trends in these three molecules is the aromaticity. There are four rules to satisfy aromaticity. (a) The molecule must be cyclic, (b) Every atom in the molecule must be conjugated, and should have uninterrupted pi-electron cloud, (c) The molecule must satisfy the Hückel's rule [4n + 2] π-electrons, *the readers must bear in mind that the number "n" comes from Algebra and not from Chemistry*, (d) The molecule must be planar. The molecules which satisfy these four conditions are stable [6]. They have an extremely high resonance energy (36 kcal/mol for benzene) undergo substitution rather than addition reactions and have delocalized pi-electrons. Benzene satisfies all these and is more stable than Cyclopentadiene and Cycloheptatriene. Hence Cyclohexatriene (Benzene) is less acidic.

Looking at the anions of these three molecules, Cyclopentadiene and Cycloheptatriene anions are more stable than the benzene anion. Because Cyclopentadiene anion is highly aromatic, planar and has odd number of pairs of pi-electrons and satisfies the Hückel's rule [4n+2] π-electrons with n = 1. It has a very high resonance energy of 42 kcal/mole [7,8]. It is quite stable by virtue of its resonance structures as shown in Figure 2. Therefore, its conjugate acid is stronger than cyclohexatriene.

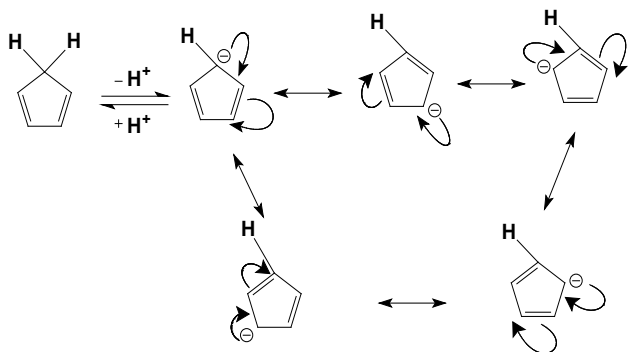


Figure 2.

Cycloheptatriene anion does not follow the Hückel's rule of aromaticity due to the presence of even number of pairs of pi-electrons. And it is anti-aromatic. Yet its conjugate acid is stronger than cyclohexatriene due to its many resonance structures as shown in Figure 3 as

they contribute their share for stability of cyclohexatriene anion.

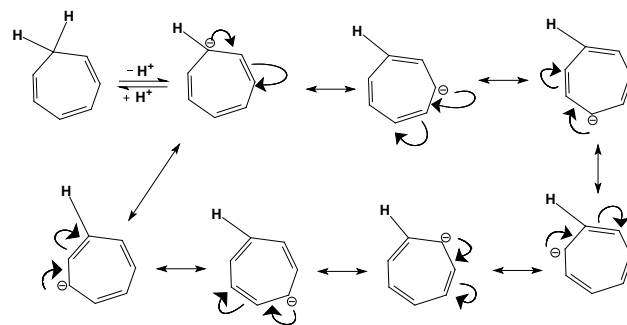


Figure 3.

The case of cyclohexatriene anion is quite different. In the cyclohexatriene anion the carbon with lone pair is already contributing its p orbital with pi-electron to the ring pi-system. It is just as same as now called as "benzene". The lone pair of the anion is at 90° to the plane of the pi-system as shown in Figure 4 [9,10]. The lone pair does not contribute to the aromaticity and is away from the pi-electron cloud and prone to be protonated easily. Here it reminds the differences of pyrrole type nitrogen (-NH-) and pyridine type nitrogen (=N-) in imidazole. The lone pair of electrons of pyrrole type nitrogen participates in the aromaticity of imidazole is not basic and is not protonated. Whereas pyridine type nitrogen is basic, and its lone pair of electrons is away from the pi-electron cloud and are prone to be protonated [11]. Therefore, conjugate acid of cyclohexatriene anion i.e., benzene is a weaker acid than either cyclopentadiene or cycloheptatriene.

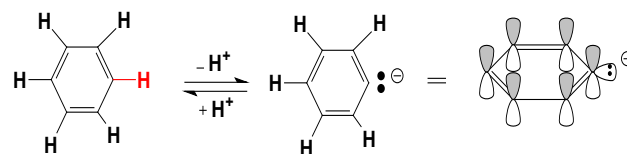


Figure 4.

Now why cycloheptatriene is a weaker acid than cyclopentadiene is a question. It was pointed out by Hückel [12] that according to the molecular orbital theory a species having [2 + 4n] pi-electrons the cycloheptatrienylium cation (Figure 5A) should be more stable than the cyclopentadienylium cation (Figure 5B). Therefore, with this analogy the stability of the anions, C₇H₇⁻ and C₅H₅⁻, should be reversed. As a result, cyclopentadiene anion (Figure 6A) with [2 + 4n] pi-electrons should be more stable than cycloheptatriene anion (Figure 6B). Therefore cyclopentadiene (pK_a = 15) is a stronger acid than cycloheptatriene (pK_a = 36).

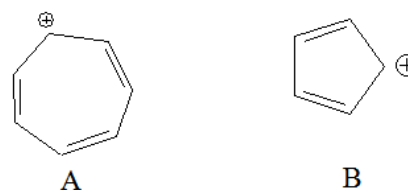


Figure 5.

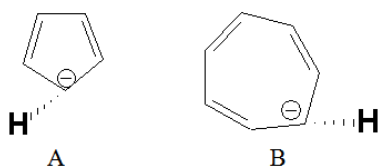


Figure 6.

Statement of Competing Interests

The authors don't have any conflict of interest.

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