Self Test Question

Rank the following acids in order of increasing acidity.

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E. d, b, a, c, e

There are a number of structural features which effect the pKa of an acid: a) Electronegativity; b) The strength of the bond to the acidic hydrogen atom; c) Inductive effects; d) Resonance delocalization in conjugate base. Remember that the ionization of an acids (HA) to a proton (H+) and conjugate base (B-) is a chemical reaction and therefore governed by the rules of thermodynamics - those factors which stabilize the conjugate base, the product of this reaction, will increase the equilibrium of this process and result in a *smaller* pKa (i.e. a more acidic HA). Similarly, factors which facilitate the breaking of the X-H bond will also increase the acidity of HA.

The answer to the question above of **B**:

- **e** Amines (**e**) are the least acidic acids of the group drawn above: amide anions (R2N-) are the least stable of the conjugate bases drawn above since nitrogen, being less electronegative than oxygen, is less able to bear the negative charge. N-H bonds are also stronger than O-H bonds.
- **a** vs. **c** phenols (**a**) are more acidic than alcohols (**c**) because the phenoxide anion generated upon proton loss is stabilized by resonance (charge can be distributed throughout the aromatic ring draw this to confirm). The the negative charge on the alkoxide anion generated upon ionization of an alcohol is localized at the oxygen atom.
- **d** vs. **b** by virtue of a weaker S-H bond, thiocarboxylic acids are more acidic that carboxylic acids (**b**). Both carboxylic acids are more acidic than the other acids because of the resonance stability present in the carboxylate ions generated upon proton loss.

Self Text Question

Which is the *most* acidic proton in the molecule below?

A. a

B.b

C. c

D. d

E. e

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