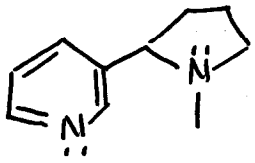
Corrections/Amplifications to Class on Friday 4/8

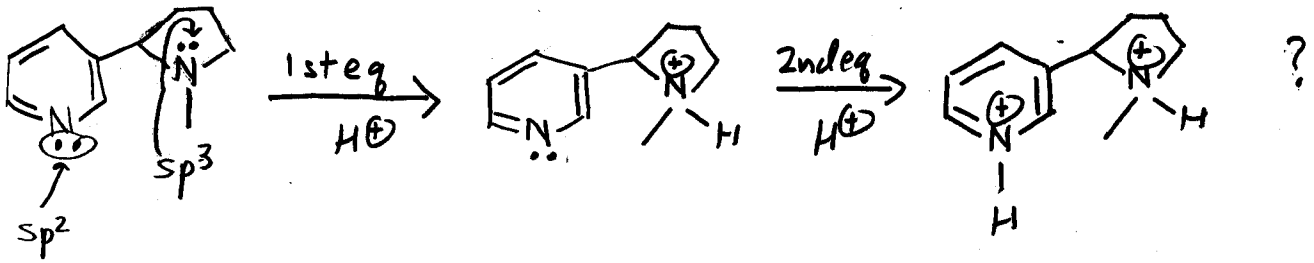
(1) So, which N on nicotine is more basic?



↑ this lone pair is <u>not</u> conjugated to a double bond (and ∴ <u>cannot</u> be delocalized) because the lone pair is in an sp^2 hybrid orbital lying in the plane of the molecule ... that is, lying in the plane of the molecule ... that is, lying in the planar <u>node</u> of the π orbitals (the double bonds). This means that there can be (at least as a first approximation) <u>no</u> coupling between the lone pair and the double bond!

(thanks to Kara for the comment!)

So, how do we explain the fact that ...



Hybridization! Since the <u>localized</u> lone pair on the left is sp^2 (vs. sp^3) hybridized, the left lone pair has a greater percentage of s character. Recall from General (or Advanced Inorganic) Chemistry that s orbitals are more stable than p orbitals because they penetrate better to the nucleus. More stable (i.e. lower energy) electron pairs are less likely to form bonds to $H^{\oplus}$.

(2) So, what's a more accurate estimate of the pH at the 1st half-equivalence point ($\frac{1}{2}V_{e_1}$)?

0.100 M B (10.0 mL) + 0.100 M HCl

	B	+ H^+	→	BH^+	$K >> 1$
I (eq)	1	$\frac{1}{2}$		0	
F (eq)	$\frac{1}{2}$	0		$\frac{1}{2}$	

Harris stops here and says

$$pH = pK_2 + \log \frac{[B]}{[BH^+]} = pK_2 = \boxed{7.85}$$

($\log \frac{[B]}{[BH^+]} \to 0$, since $[B] = [BH^+] = 1$)

But one could go one step further and consider hydrolysis:

	B + H_2O ⇌	BH^+ +	OH^-
I	F′	F′	0
C	−X	+X	+X
E	F′−X	F′+X	X

where $F' = \frac{1}{2}(0.100\,M)\left(\frac{10.0\,mL}{15.0\,mL}\right) = 0.0333_3\,M$

(thanks to Khizar!)

$$K_{b_1} = \frac{(0.0333_3 + x)(x)}{0.0333_3 - x} = 7.0_8 \times 10^{-7}$$

$$x^2 + 0.0333_3 x = -7.0_8 \times 10^{-7} x + 2.3_6 \times 10^{-8}$$

$$x^2 + 0.0333_{307} x - 2.3_6 \times 10^{-8} = 0$$

Quad formula ⇒ $X = [OH^-] = 7.0_8 \times 10^{-7}\,M$ ⇒ $\boxed{pH = 7.85}$

SAME!