CHEM*1040 FINAL EXAM PREPARATION PROBLEMS LAB - ANSWERS FALL 2014

1. The boxes below contain a series of 0.1 M aqueous solutions of increasing pH where 1 is the solution of lowest pH and 6 is the solution of highest pH.

1	2	3	4	5	6

Match each compound below with the correct numbered box.

aniline, pK_b = 9.38 **(5)** nitric acid **(1)** pyridine, pK_b = 8.75 **(6)**
HClO, pK_a = 7.53 **(2)** sodium nitrate **(4)** phenol, pK_a = 9.89 **(3)**

Solution: Sort each into categories of "acids", "bases" and "neutrals", *i.e.*, **ACIDS**: nitric acid – Strong Acid (SA); HClO – Weak Acid (WA) & phenol – WA; **BASES**: aniline – Weak Base (WB) & pyridine – WB; **NEUTRAL** (N): sodium nitrate. Next, sort the acids from strongest acid to weakest acid. Note: Smaller pK_a value = lower pH = stronger acid and larger pK_a = higher pH = weaker acid. Place any neutral salts after weakest acid. Lastly, sort bases from weakest base (lower pH = largest pK_b) to strongest base (highest pH = smallest pK_b). *(Text Ref: Sections 4.4, 16.1, 16.3-16.4)*

Answer: nitric acid < HClO < phenol < sodium nitrate < aniline < pyridine

2. Which of the following pairs of ions **cannot** exist together in high concentrations in aqueous solution?

A) NH_4^+ & Br^- WA + N
B) Li^+ and OH^- N + SB
C) H_3O^+ & NO_3^- SA + N
D) K^+ and F^- N + WB
E) H_3O^+ & $HCOO^-$ **SA + WB**

If the ions cannot exist together, they will react! Neutral species do NOT react with other species, so look for an acid plus base combo, *i.e.*, a titration reaction. *(Reference: Sections 4.4, 16.4)*

3. Which one of the following soluble salts gives an acidic aqueous solution? *(Ref: Sect'n 16.4)*

A) $CH_3NH_3NO_3$ **$CH_3NH_3^+$(WA)**; NO_3^-(N)
B) $LiNO_2$ Li^+(N); NO_2^-(WB)
C) $NaHCO_3$ Na^+(N); HCO_3^-(WB)
D) $Mg(ClO_4)_2$ Mg^{2+}(N); ClO_4^-(N)
E) $KC_6H_5CO_2$ K^+(N); $C_6H_5CO_2^-$(WB)

4. Find the pH of a 0.79 M aqueous solution of *sodium benzoate*. The K_a for benzoic acid is 6.5×10^{-5}.

Solution: Sodium benzoate is a basic salt; ∴ solution will be basic! Benzoic acid is its conjugate acid. *(Ref: Sect'n 16.4)*

NIE: $C_6H_5COO^-(aq) + H_2O(l) \rightleftharpoons C_6H_5COOH(aq) + OH^-(aq)$; $K_b = K_w/K_a = 1.0\times10^{-14}/6.5\times10^{-5} = 1.5\times10^{-10}$

$0.79 - x$ x x $[OH^-] = x = \sqrt{\{K_b \times (0.79 - x)\}}$

Assume $x << 0.79$; ∴ $x = \sqrt{\{1.5\times10^{-10} \times 0.79\}} = 1.1\times10^{-5}$; pOH = $-\log(1.1\times10^{-5})$ = 4.96; **pH** = 14.00 – 4.96 = **9.04**

5. Calculate the pH of a solution prepared by dissolving 0.382 mol ammonia and 0.185 mol HBr in enough water to produce 0.750 L of solution. The pK_b of ammonia is 4.74. **Rxn is a WB + SA – set up ICE table.**

A) 8.95 B) 9.57 C) 9.29 D) 9.23 E) 5.05 *(Ref: Sect'n 16.6)*

Answer: NIE: $NH_3(aq) + H_3O^+(aq) \rightleftharpoons NH_4^+(aq) + H_2O(l)$; $pK_a = 14.00 - pK_b = 9.26$

	NH_3	H_3O^+	NH_4^+	H_2O
I	0.382	0.185(LR)	0	
C	-0.185	-0.185	+0.185	
E	0.197	0	0.185 Buffer sol'n	

$pH = pK_a + \log\{[\text{conj. base}]/[\text{cong. Acid}]\}$ H-H eq'n

$pH = 9.26 + \log\{ n_{NH_3} / n_{NH_4^+} \}$

pH = 9.26 +log{0.197/0.185} = **9.29**

6. The following compounds are available as 0.10 M aqueous solutions.

A) $HClO_4$ B) aniline C) HCN
D) RbOH E) methylamine F) HClO
G) $HClO_2$ H) $NaClO_2$ **OR** I) triethylamine

Pick two solutions that could be used to prepare a buffer with a pH of 10.8. *(Ref: Sect'n 16.6)*

Solution: The *effective pH range* for any buffer is **$pK_a \pm 1$**. Therefore, one must find a species (or its conjugate) that has a pK_a value between 9.8 and 11.8, *i.e.*, pK_b for methylamine (CH_3NH_2) is 3.44, so its conjugate acid has a pK_a of 10.56 (=14.00 – 3.44). To form the conjugate acid of methylamine, we add a strong acid, such as $HClO_4$. Therefore, if **$HClO_4$ and methylamine** are mixed in the correct ratio (*i.e.*, 1:1.74 from H-H eq'n), a buffer solution can be prepared, having a pH of 10.8. A 2nd option is **triethylamine** (pK_b = 3.00 & pK_a for $(C_2H_5)_3NH^+$ = 11.00) **+ $HClO_4$** at a ratio of 0.63:1, respectively.

7. If **65.0 mL** of a solution containing **0.10 M NaCN(aq) and 0.10 M HCN(aq)** has 4.0 mL of 0.40 M NaOH(aq) added to it, calculate the **change in pH** of the solution (*i.e.*, $pH_{Final} - pH_{Initial}$). The pK_a of HCN is 9.31.

A) +1.2 B) +0.22 C) +0.12 D) –0.12 E) –0.22 *(Ref: Sect'n 16.6)*

Solution: NIE: $OH^-(aq) + HCN(aq) \rightleftharpoons H_2O(l) + CN^-(aq)$; $pH = pK_a + \log\{CN^-/HCN\}$ **H-H eq'n for buffer sol'n**

I	1.6×10^{-3} **(LR)**	6.5×10^{-3}	6.5×10^{-3}	moles	$pH_{Initial} = pK_a = 9.31$ for **1:1 buffer (b/c log term = 0)**
C	-1.6×10^{-3}	-1.6×10^{-3}	$+1.6\times10^{-3}$	moles	$pH_{Final} = 9.31 + \log\{8.1\times10^{-3}/4.9\times10^{-3}\}$
E	0	4.9×10^{-3}	8.1×10^{-3}	moles	$pH_{Final} = 9.31 +$ **0.22** $= 9.53$; **ΔpH = +0.22**

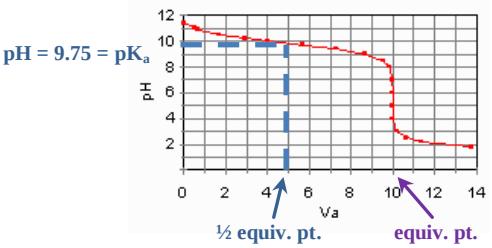
8. Calculate the equilibrium constant for the reaction that occurs when hydrochloric acid is added to the buffer B(*aq*)/BHCl(*aq*). The K_b of B is 6.7×10^{-5}.

Solution: **NIE:** $H_3O^+(aq) + B(aq) \rightleftharpoons H_2O(l) + BH^+(aq)$; $K_b = 6.7\times10^{-5}$; $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$

& $K_a = K_w/K_b = 1.0\times10^{-14}/6.7\times10^{-5} = 1.5\times10^{-10}$; $BH^+(aq) + H_2O(l) \rightleftharpoons B(aq) + H_3O^+(aq)$

Comparing the NIE for the reaction with the two chemical equations that go with the definitions of K_b and K_a, one sees that the NIE is the reverse of the K_a chemical equation. The equilibrium constant for the NIE is therefore K_a^{-1} or $1/1.5\times10^{-10} =$ **6.7×10^{9}** NOTE: A rxn b/w an acid & a base (in this case a SA + WB) will **always** produce a large K value, as these species cannot exist in large quantities together. They will react to form products that are more stable than the reactants. *(Ref: Sect'n 16.1, 16.3-16.4 & 16.7)*

9. The titration curve for 10.0 mL of a 0.100 M weak base with 0.100 M HI(aq) is given below.



i) Estimate the pK_b for this weak base

ii) Identify the weak base. *(Ref: Sect'n 16.6-16.7)*

Solution: i) First determine the pK_a for the conjugate acid, through finding the pH at the ½-equivalence point, *i.e.*, location of 1:1 buffer where $pH = pK_a$. The equivalence point is located at 10 mL, so the ½-equivalence is at 5 mL or pH = 9.75. ∴ **pK_b** = 14.00 – 9.75 = **4.25**.

ii) A weak base having a $pK_b \cong 4.25$ is **trimethylamine, or $(CH_3)_3N$.**

10. For the titration of 50.0 mL of 0.0200 M HClO(aq) with 0.100 M NaOH(aq), which of the following indicators should be used for this titration? Determine the pH of the solution to support your answer.

A) methyl orange ($pK_{In} = 3.4$)
B) methyl red ($pK_{In} = 5.0$)
C) litmus ($pK_{In} = 6.5$)
D) thymol blue ($pK_{In} = 9.3$)
E) alizarin yellow R ($pK_{In} = 11.2$)

(Ref: Sect'n 15.8 & 16.7)

Solution: NIE: $HClO(aq) + OH^-(aq) \rightleftharpoons ClO^-(aq) + H_2O(l)$; 50.0 mL of 0.0200 M HClO = 1.00×10^{-3} moles HClO

I	1.00×10^{-3}	1.00×10^{-3}	0	moles	To reach E.P.: $V_{NaOH} = 1.00\times10^{-3}$ moles/0.100 M = 0.0100 L
E	0	0	1.00×10^{-3}		Total volume = 50.0 mL + 10.0 mL = 60.0 mL

The conjugate base ClO^- is formed during this titration. Therefore, the pH at the equivalence point will be basic. To find the exact pH, determine the pH of the solution once equilibrium has been reached after the addition of equal moles of HClO and NaOH, *i.e.*,

1.00×10^{-3} mol ClO^- in 60.0 mL = 0.0167 M

NIE: $ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$ $K_b = K_w/K_a(HClO) = 1.0\times10^{-14}/3.5\times10^{-8}$

I	0.0167	0	0	moles	$K_b = 2.9\times10^{-7}$
E	$0.0167 - x$	x	x		$[OH^-] = x = \sqrt{\{K_b \times (0.0167 - x)\}} \cong \sqrt{\{K_b \times 0.0167\}}$

$[OH^-] = 6.95\times10^{-5}$; $pOH = -\log[OH^-] = 4.16$; $pH = 9.84$

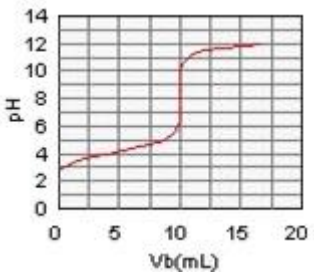
Knowing the pH of the solution is 9.8, then an appropriate indicator would have a pK_{In} value between 7.8 – 10.8. Therefore, **thymol blue** would be appropriate.

11. The equilibrium constant for the reaction of a strong acid with a strong base is 1×10^{-14}. True or False?

$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$; $K_w = 1\times10^{-14}$;

Rxn: $H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$; $1/K_w =$ **$1\times10^{+14}$** acid + base = large K value! ∴ favours products! *(Ref: Section 16.7)*

12. For the titration of 50.0 mL of 0.0200 M $C_6H_5COOH_{(aq)}$ with 0.100 M $NaOH_{(aq)}$ is given below.



What is/are the major species in the solution after the addition of

i) 0 mL of $NaOH_{(aq)}$? only **weak acid** present **∴A)** *(Ref: Sect'n 16.7)*

ii) 6.0 mL of $NaOH_{(aq)}$? within **buffer** region **∴E)**

iii) 10.0 mL of $NaOH_{(aq)}$? equiv. pt. where only **conj. base** present **∴F)**

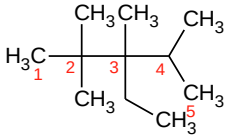
iv) 15.0 mL of $NaOH_{(aq)}$? past the equiv. point with excess OH^- **∴D)**

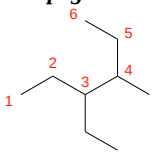
NIE: $C_6H_5COOH_{(aq)} + OH^-_{(aq)} \rightleftharpoons C_6H_5COO^-_{(aq)} + H_2O_{(l)}$

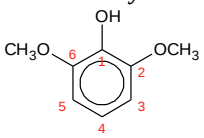
A) C_6H_5COOH
B) C_6H_5COOH and H_3O^+
C) C_6H_5COOH and OH^-
D) OH^- and $C_6H_5COO^-$
E) C_6H_5COOH and $C_6H_5COO^-$
F) $C_6H_5COO^-$

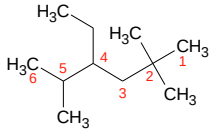
13. Name the following compounds.

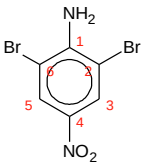
Refer to pages 7-13 in CHEM*1040 Organic Chemistry Notes (ON).

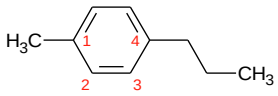
i)

3-ethyl-2,2,3,4-tetramethylpentane

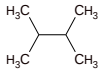
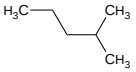
ii)

3-ethyl-4-methylhexane

iii)

2,6-dimethoxyphenol

iv)

4-ethyl-2,2,5-trimethylhexane

v)

2,6-dibromo-4-nitroaniline

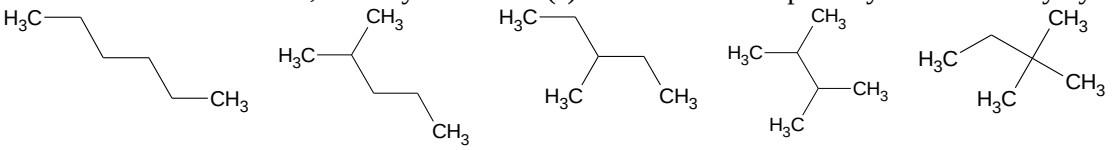
vi)

p-propyltoluene
or 4-propyltoluene

14. The compounds 2,3-dimethylbutane and 2-methylpentane are   Ref: ON p. 2, 23-24 & 28

Solution: Both structures have formula C_6H_{14}. They are both alkanes, but have different parent names, so they are:

A) functional isomers (B) structural isomers C) geometrical isomers D) diastereoisomers

15. From the structures below, identify the isomer(s) that have ONLY primary and secondary hydrogens.

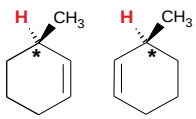


i) ii) iii) iv) v)

Solution: Primary (1°) hydrogens are bonded to a 1° carbon – a carbon atom that is bonded to only one other carbon, *i.e.*, terminal carbons. Secondary (2°) hydrogens are bonded to a 2° carbon – a carbon atom that is bonded to two other carbons, *i.e.*, middle carbons in i). Tertiary (3°) hydrogens are bonded to a 3° carbon atom, e.g., structures ii), iii) & iv). A quaternary (4°) carbon is found in v). **Answer: Structures i) and v).** Ref. ON 3-4.

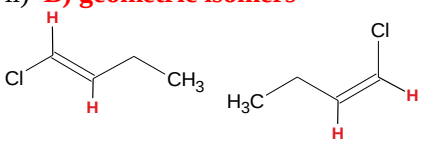
16. Indicate whether the compounds below are isomers or identical.

i) **C) enantiomers**



chiral; non-super-imposable mirror images
(see ON pp. 24-28)

ii) **B) geometric isomers**



***trans* isomer & *cis* isomer (ON p. 23-4)**

Choose from:
A) structural isomers
B) geometric isomers
C) enantiomers
D) identical
E) not isomers

17. Which of the following is most volatile? **Ethers have only 1 type of IMFs while alcohols have all 3 types (ON pp. 31-3).**

A) $(CH_3)_2C(OH)CH_3$ **2° alcohol** B) $CH_3(CH_2)_3OH$ **1°alcohol** C) $CH_3CH_2OCH_2CH_3$ **ether**

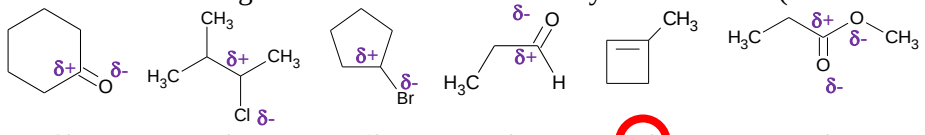
D) $CH_3CH(OH)CH_2CH_3$ **2°alcohol** E) $(CH_3)_3COH$ **3°alcohol** F) $CH_3CH_2CH(OH)CH_3$ **2° alcohol**

18. Of the following compounds, which would be expected to be the **LEAST** soluble in water? (Ref. ON p. 34)

A) $CH_3CH_2OCH_3$ B) $CH_3CH_2CH_2COOH$ C) CH_3OH D) $(CH_3)_2NH$

ether – least like H_2O **carboxylic acid** **alcohol** **amine**

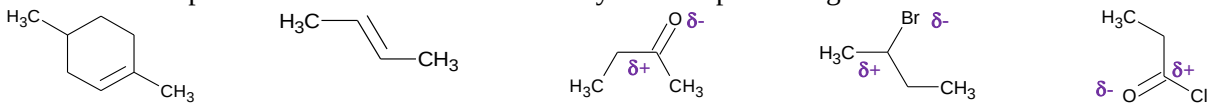
19. Which of the following would be attacked **ONLY** by a Lewis acid? (Select as many as applies.)



A) B) C) D) E) F)

SOLUTION: Lewis acids, or electrophilic agents, look for a source of electrons (*e.g.*, π e$^-$s); would attack A, D, E & F. Lewis bases, or nucleophilic agents, look for a positive charge from a dipole moment; would attack A, B, C, D and E. Out of A, D, E & F, **only E** would not also be attacked by a Lewis base. (Ref.: ON p 35)

20. Which of the compounds below would be attacked by a nucleophilic reagent?

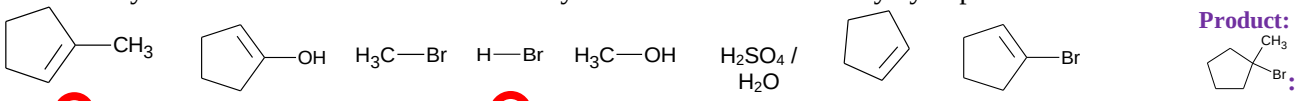


1 2 3 4 5

A) 2, 3, and 5 B) 4 only C) 3, 4, and 5 D) 1, 2, 3, and 5 E) 1 and 2

Nucleophilic reagents look for dipoles, where they will attack the positively charge carbon atom, *i.e.*, "nuclei" (ON p.35).

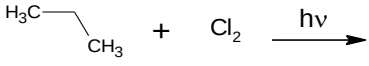
21. Identify which reactants would be used to synthesize 1-bromo-1-methylcyclopentane? **Ref: ON 39-40.**



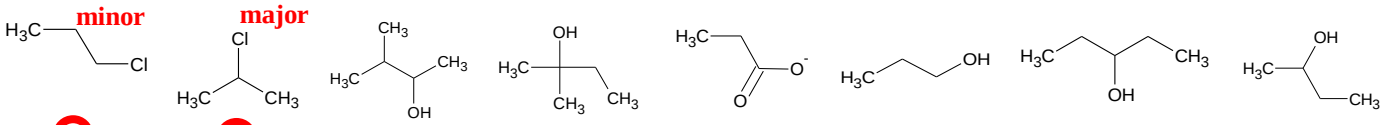
1 2 3 4 5 6 7 8

Electrophilic additions add H's to the side of the double bond that has the most H's.

22. What are the minor & major products for the following:



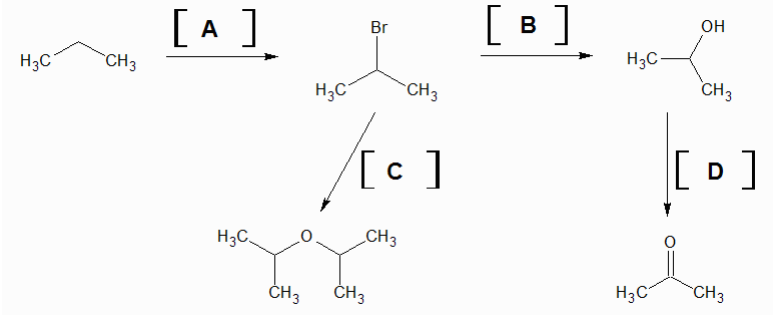
? substitution rxn



1 2 3 4 5 6 7 8

Rxn = free radical halogenation; reactivity prefers 3°H > 2°H > 1° H's. Minor product = 1 & MAJOR Product = 2; Ref: ON 35-38.

23. Complete the reactions below by identifying the missing species in the space provided. Also identify the functional group of the ***reactant*** given and the type of reaction (*i.e.*, substitution, addition, oxidation or reduction).



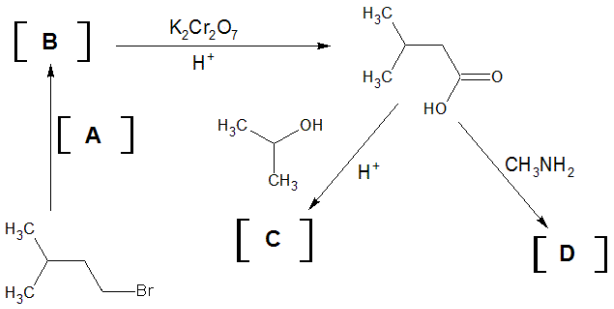
A: **Br_2/hν**; alkane; substitution (p. 36-38)

B: **OH^- (or NaOH)**; alkyl halide; substitution (p. 42-43)

C: **$^-OCH(CH_3)_2$**; alkyl halide; substitution (p. 42-43)

D: **$Cr_2O_7^{2-}/H^+$**; 2° alcohol; oxidation (p. 44)

24. Complete the reactions below by identifying the missing species in the space provided. Also identify the functional group of the ***product*** and the type of reaction (*i.e.*, substitution, addition, oxidation or reduction).



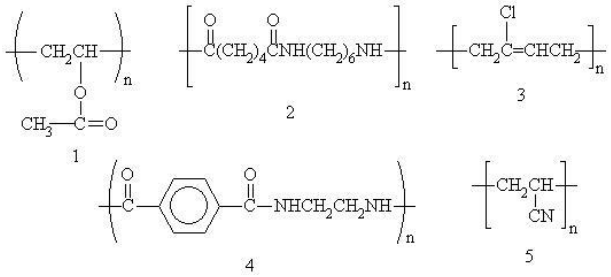
A: **OH^- (or NaOH/KOH); alcohol; substitution**
Ref: ON p. 42-43

B: **$(CH_3)_2CHCH_2CH_2OH$; carboxylic acid; oxidation**
Ref: ON p. 44

C: **$(CH_3)_2CHCH_2C(O)OCH(CH_3)_2$; ester; substitution**
Ref: ON p. 48

D: **$(CH_3)_2CHCH_2C(O)NHCH_3$; amide; substitution**
Ref: ON p. 48-52

25. Classify each of the following polymers as either an addition or condensation polymer.



1) **addition polymer** **Ref: ON p. 40-42**
2) **condensation polymer** **Ref: ON p. 49-51**
3) **addition polymer**
4) **condensation polymer**
5) **addition polymer**

DATA: $K_w = 1.0\times 10^{-14}$ at 25°C

Acidity and Basicity Constants (25°C)

Acid	K_a	pK_a	Base	K_b	pK_b
$HClO_2$	1.0×10^{-2}	1.92	$(C_2H_5)_3N$	1.0×10^{-3}	3.00
HNO_2	4.3×10^{-4}	3.37	$(CH_3)_2NH$	5.6×10^{-4}	3.25
HF	3.5×10^{-4}	3.46	CH_3NH_2	3.6×10^{-4}	3.44
HCOOH	1.8×10^{-4}	3.74	$(CH_3)_3N$	6.5×10^{-5}	4.19
CH_3COOH	1.8×10^{-5}	4.74	NH_3	1.8×10^{-5}	4.74
HClO	3.5×10^{-8}	7.46	C_5H_5N (pyridine)	1.8×10^{-9}	8.74
HCN	4.9×10^{-10}	9.31	$C_6H_5NH_2$ (aniline)	4.3×10^{-10}	9.37