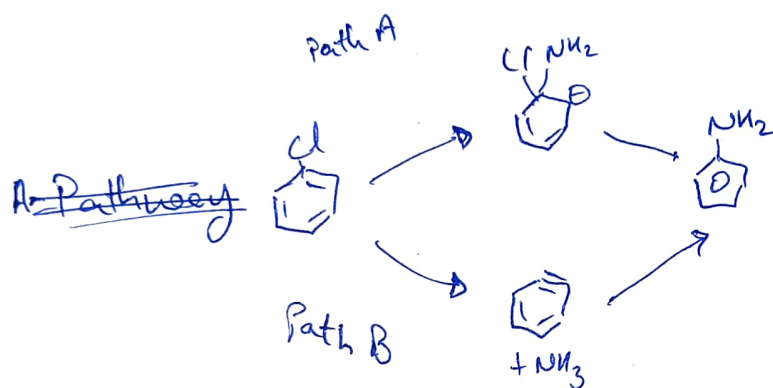


2020CH10071

ADITYA GAUTAM

Part - 2

Ans 1



3 expt

Expt 1

Activation parameter by Eyring's plot.

Plotting Eyring's plot and solving slope and intersection gives  $\Delta S$  for both paths the observation will be

Path A  $\rightarrow \Delta S < 0$  and large magnitude.

(Reason: due to  $\downarrow$  in entropy as 2 free molecule combine)

Path B  $\rightarrow \Delta S = 0$

or may be small +ve (owing to free Cl released)

Expt 2

Hammett plot  $\rightarrow$   $\rho$  values.

Path A  $\rightarrow \rho > 0$  and  $|\rho| \approx 4$ -ish  
(owing to ~~large~~ -ve charge generation in aromatic ring)

Path B  $\rightarrow \rho$  close to zero  
 $\checkmark$  (no charge build up in TS)

Expt 3

KIE effect based on C-H / C-D bond

Path A  $\rightarrow \frac{k_{CH}}{k_{CD}} = 1$   $\rightarrow$  no KIE as C-H bond is not affected in the pathway.

Path B  $\rightarrow \frac{k_{CH}}{k_{CD}} > 1$  and  $\approx 3.4$ -ish

6  $\checkmark$  as PKIE; as the C-H/D bond breaks in RDS  
testable of the shown "Benzynes Mech<sup>n</sup>"

~~Expt 4~~ Note 1  $\rightarrow$  Rate law ~~can't be different~~ can't be used as in both Paths

$$\text{Rate} = k [\text{chlorobenzene}]^1 [\text{NH}_2^-]^1$$

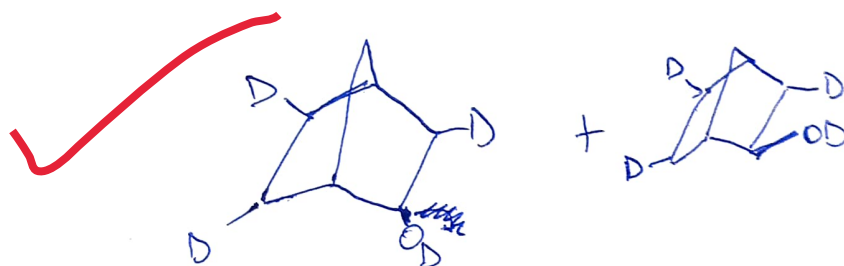
Note 2  $\rightarrow$  If we do a very precise expt. then  
the KIE of C-<sup>35</sup>Cl/<sup>37</sup>Cl may also tell diff.  
as in Path A  $\rightarrow$  no C-Cl KIE observed.  
Path B  $\rightarrow$  yes

Ans 2

(a) mech<sup>n</sup>



3

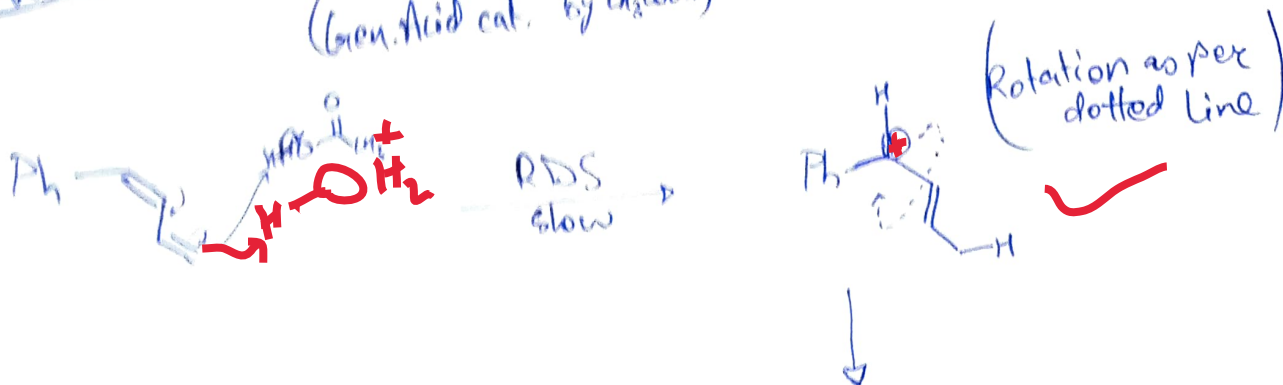


→ Thus a mix of endo and exo product.

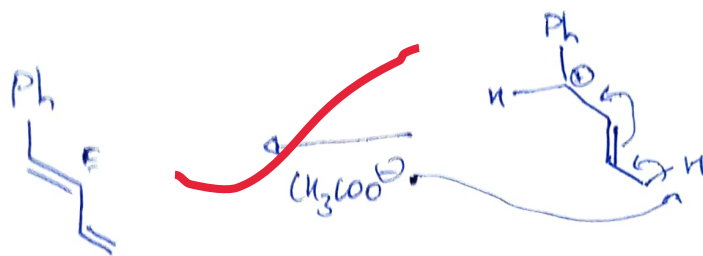
(b) as the RDS involve C-D/H bond breakage  
 thus it'll show PKI  $\Rightarrow \frac{k_H}{k_D} \approx 5$  ish  
 (as given)

Ans 3

(Gen. Acid cat. by  $\text{CH}_3\text{COOH}$ )



3



3 expt to verify

expt ① → Hammett plot → large -ve  $\rho$  value ~~ish~~ (-4 ish)  
(as there is +ve charge format<sup>n</sup> in ~~the~~ conjugation in ring)

expt ②

$$\frac{k_{\text{O-H}}}{k_{\text{O-D}}} \approx (3-4) \text{ ish}$$

3

as the O-H/D bond is broken in RDS  
thus ~~PKIE~~ PKIE should be observed & thus the values.

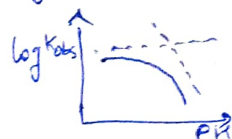
expt ③

→ Rate Law =  $K [\text{Ph-CH=CH}_2]^1 [\text{CH}_3\text{COOH}]^1$

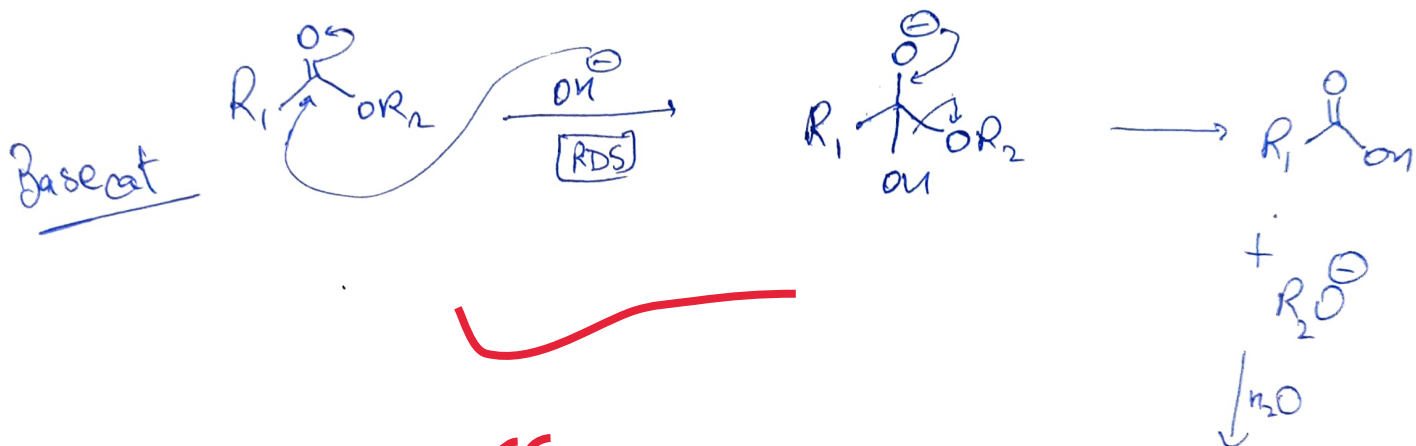
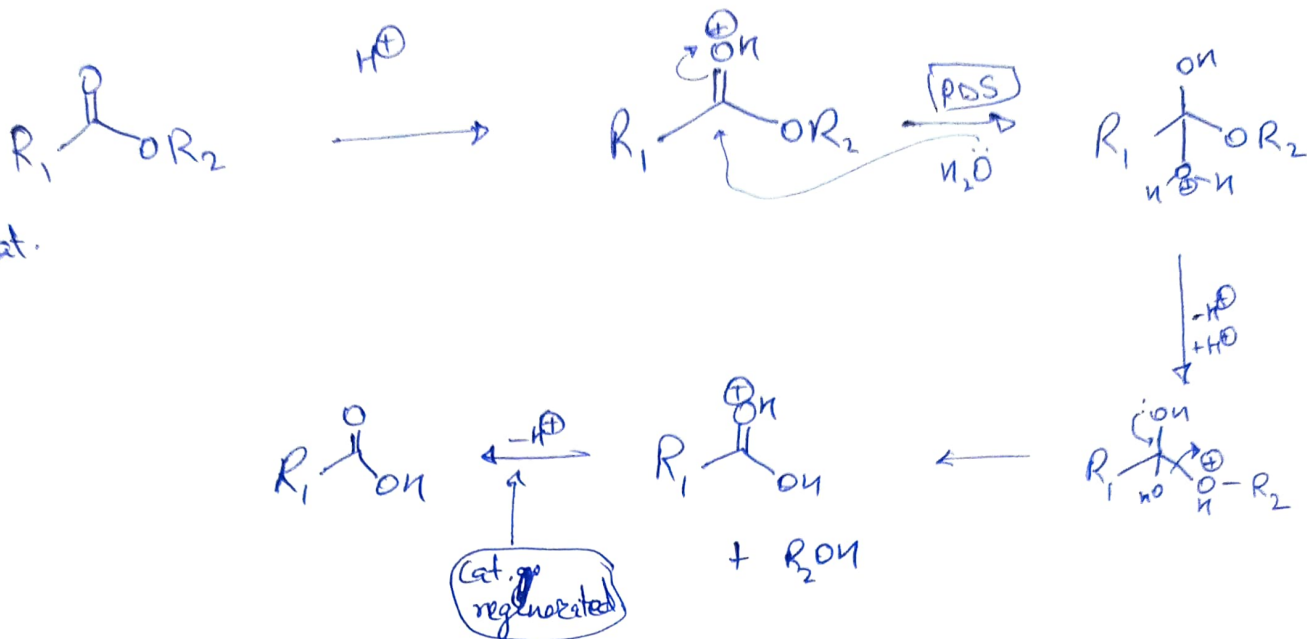
+ as both species are part of RDS. (thus Gen. Acid cat.)

expt ④

{ plots of  $\log(k_{\text{obs}})$  vs  $\log[\text{CH}_3\text{COOH}]$  will be }  $K_{\text{obs}}$



Ans 4



No T.S.

for ethyl benzoates  $R_1 = Ph$

Clearly in acid cat.  $R_1^+$  → +ve charge already in TS (no generat<sup>n</sup>)  
 so value of  $\rho$  very close to zero.  
 (small +ve as <sup>equivalent</sup> charge enter (ie +ve spreads) due to)

2 in base cat. → large -ve charge generat<sup>n</sup> in TS  
 thus  $\rho = 2.19$  (ie large +ve)



Ans 5

for the rxn it's give  $\rho = -ve$

$\Rightarrow$  +ve charge gen. in TS

but magnitude tells no charge in conjugat<sup>n</sup>.

$\Rightarrow$   $S_N2$  mech<sup>m</sup>.

now by Hammett's ~~not~~ Lin. free energy relat<sup>n</sup>

$$\log_{10} \left( \frac{K(x)}{K(H)} \right) = \rho \sigma(x) = \rho \left( \frac{-\Delta G^\circ(x)}{2.303 RT} \right)$$

using data.

$$\text{for Br} \rightarrow \log_{10} \left( \frac{K_{Br}}{K_H} \right) = -1.31 (-0.26) \quad \text{--- (1)}$$

$$\text{for NO}_2 \rightarrow \log_{10} \left( \frac{K_{NO_2}}{K_H} \right) = (-1.31) (0.81) \quad \text{--- (2)}$$

$$\begin{aligned} \text{(1) - (2)} \Rightarrow \log_{10} \left( \frac{K_{Br}}{K_{NO_2}} \right) &= (1.31) (0.81 - 0.26) \\ &= 0.7205 \end{aligned}$$

5

$$\Rightarrow \frac{K_{Br}}{K_{NO_2}} = 10^{0.7205} = 5.254120151 > 1$$

$$\Rightarrow K_{Br} > K_{NO_2}$$

$\Rightarrow$  Rxn is faster with Br

Ans 6

by hammett's lin. free energy relat<sup>n</sup>:

$$\log_{10} \left( \frac{k_x}{k_H} \right) = \rho \sigma (X)$$

putting given values. and  $X = NO_2$

$$\Rightarrow \log_{10} \left( \frac{k_{NO_2}}{2 \times 10^{-4} \frac{M}{S}} \right) = (2.38) (0.7)$$

$$= 1.666$$

$\Rightarrow$

$$\frac{k_{NO_2}}{2 \times 10^{-4}} = 10^{1.666}$$

3

$$\Rightarrow k_{NO_2} = 92.689 \times 10^{-4} \frac{M}{S}$$

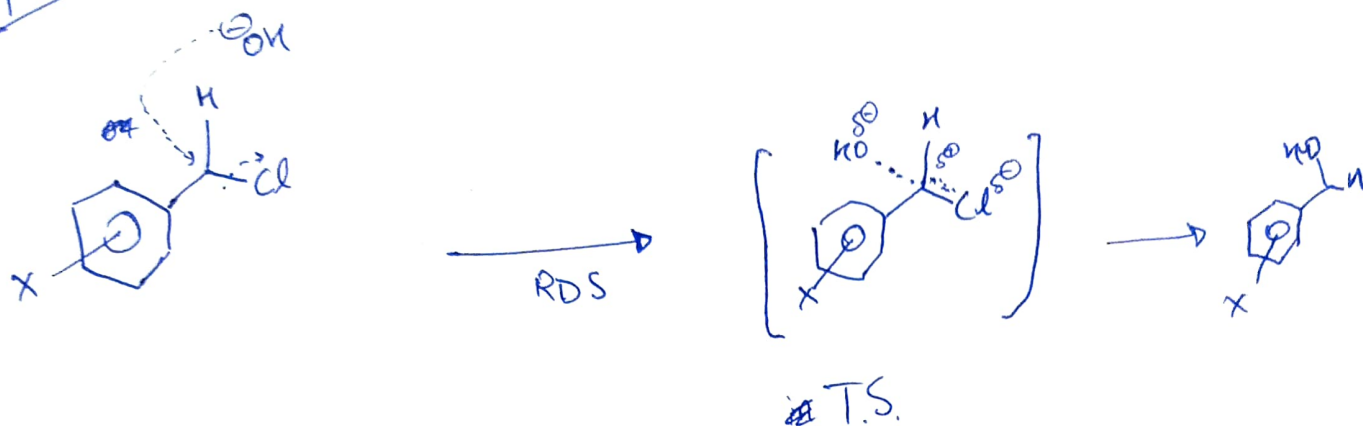




Ans 8

4

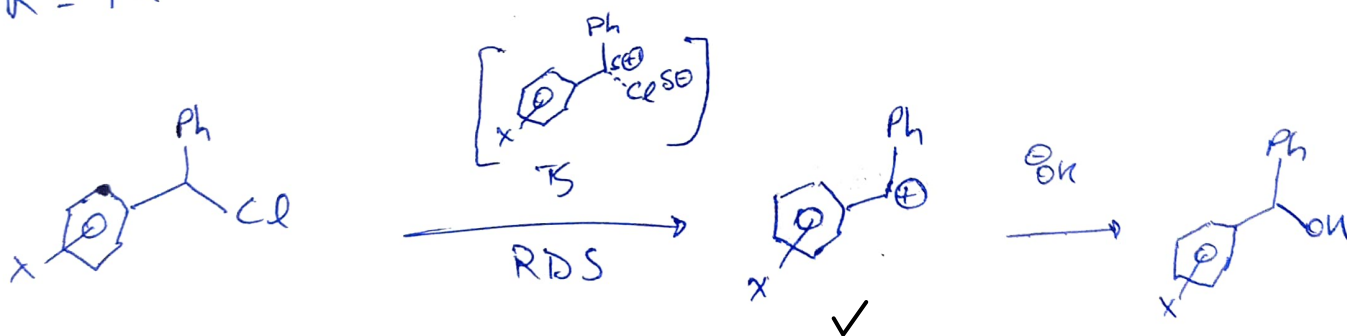
R=H



Note the  $R_X^m$  was by  $S_N2$  mech. ✓

and ~~the~~ charge wasn't generated in TS  
 (or small +ve) thus expected  $\rho = 0$  ✓  
 (or small -ve)

if  $R = Ph$



not ~~the~~ the mech<sup>m</sup> was  $S_N1$

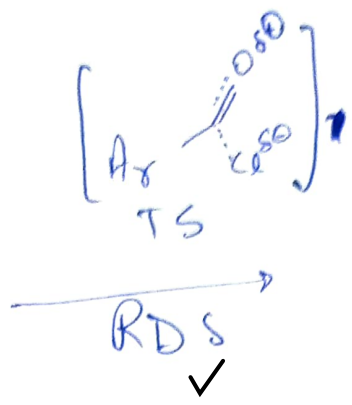
clearly large +ve charge format<sup>n</sup> took place in TS  
 and it was in conjugat<sup>n</sup> with aromatic ring  
 (having x) thus expected  $\rho = -ve$  and large (side)

thus the observation. ✓

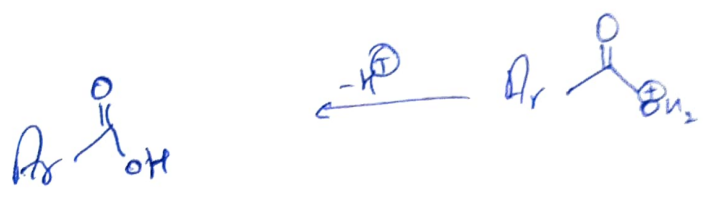
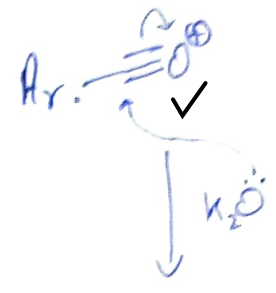
Ans 9  
6

2 mech<sup>m</sup>

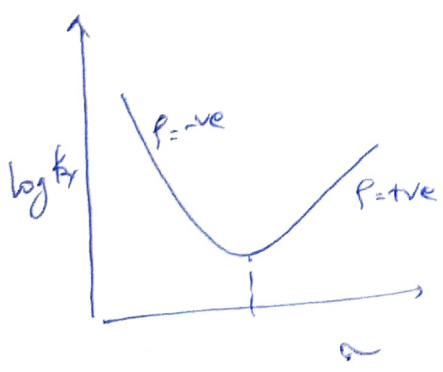
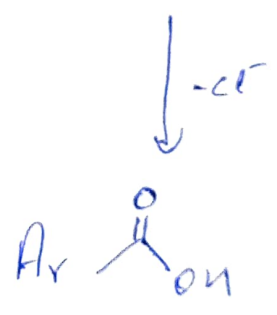
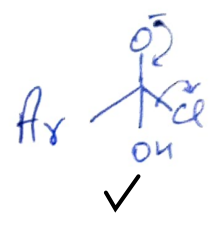
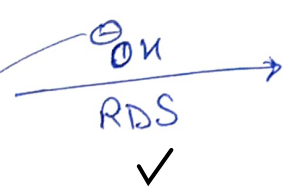
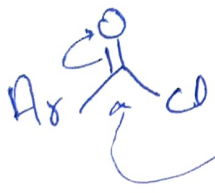
way ①



(as Cl<sup>-</sup> is good leaving group and trace of EDG will stabilize intermediate)



way ②



in way ① → large +ve charge gen. near ring in TS  
 thus  $\rho = -ve$  is  $\rho = -ve$   
 charge not in conjugation →  $\rho = -ve$

in way ② → -ve charge format<sup>n</sup> in TS  
 thus  $\rho = +ve$

note for a large  $\Rightarrow X = \text{EWG}$   $\Rightarrow$  TS of way ① is ~~unstable~~ <sup>unstable</sup>  
 $\Rightarrow$  mech<sup>m</sup> ② is preferred.

a low  $\Rightarrow X = \text{EDG}$   $\Rightarrow$  TS of way ① is stabilized.  
 $\Rightarrow$  mech<sup>m</sup> ① is preferred.

→ and thus as  $\alpha$  changes

→ the mechanism followed changes.

→ thus  $p$  values changes

→ thus slope changes

→ thus plot varies

→ thus nonlinear Plot of  $\log k$

→ thus the observation!