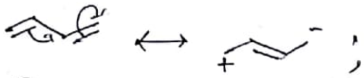
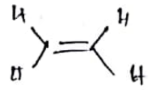
UVS-1

- λ_{max} value for ethylene and 1,3 Butadiene are identical - Justify the statement.

Ans. The statement is false. Ethylene is a 2π electron system and remains as non conjugated molecule, where as 1,4 butadiene is a 4π electron system. Conjugation in the later decreases the gap between the Homo & LUMO. So ethylene will absorb at a lower wavelength than that of 1,3 butadiene.



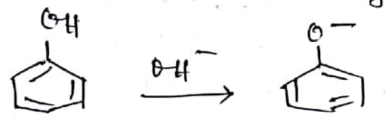
$\lambda_{max} \sim 217$ nm



$\lambda_{max} \sim 164$ nm.

Q.2. do you expect any change in position of UV absorption of Phenol in alkaline solution from its neutral solution?

Ans. There will occur a bathochromic shift when phenol is taken from neutral to alkaline solution. In neutral medium Phenol ~~abs~~ absorbs at ~210 nm. But when the medium is made alkaline Phenol remains as phenoxide ion (PhO^-). Now O^- is a better electron donor (+R group) than OH. So a better conjugation occurs in PhO^- than that of PhOH that will reduce the energy gap between Homo and LUMO. Hence phenol in alkaline medium will absorb at a higher λ_{max} value.



Phenol

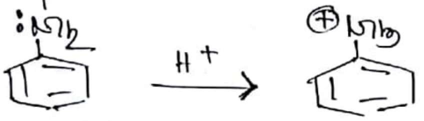
$\lambda_{max} \sim 210$ nm

Phenoxide

$\lambda_{max} \sim 235$ nm.

Q.3. The UV absorption maxima of aniline in acidic solution is almost similar to that of benzene whereas in neutral aqueous solution this is not the case - why?

Ans. The absorption of aniline is due to conjugation of the unshared electron pair on Nitrogen atom of NH_2 group with the π electron system of benzene ring. But as soon as the medium is made acidic NH_2 group is converted into $\overset{\oplus}{N}H_3$ group and there is no electron to conjugate with the benzene ring. As a result there will show a blue shift and appear as a spectrum similar to that of benzene.

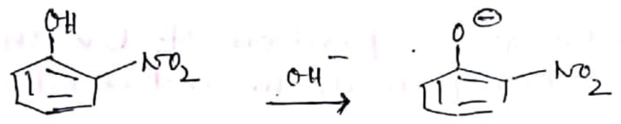


$\lambda_{max} \sim 230$ nm

$\lambda_{max} \sim 203$ nm.

Q4. Orthonitrophenol in 0·1(M) HCl shows λmax at 350nm, but in 0·1(M) NaOH solution its λmax is shifted to 415 nm - Exp

Ans. Orthonitrophenol in 0·1(M) ~~HCl~~ remains as orthonitrophenoxide ion, but ~~as~~ remains in unionised form in 0·1(M) HCl. Now O⁻ being better electron donor (+R) makes better conjugation with the benzene ring than that of ÖH group. So in case of alkaline solution there will occur sufficient lowering of energy gap between the Homo and LUMO. So the compound in 0·1 (M) NaOH solution will obviously absorb at a higher λmax value than when in acidic solution [0·1 (M) HCl].



0·1(M) HCl

?? λmax 350nm.

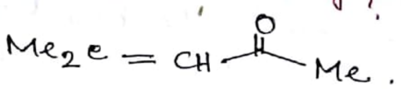
0·1 (M) NaOH

λmax · 415 nm

Q.5. Acetone ~~absorbs~~ two λmax values; at 280 nm (ϵ ~15) and 190 nm (ϵ ~10000. Identify the electronic transitions and explain why one of them is more intense.

Ans. Acetone possesses a Carbonyl Chromophore. The possible electronic transitions are n→π* and π→π*. But the n→π* ~~transition~~ is lowest energy transition, so the longest wavelength at 280 nm corresponds to n→π* transition. This is a very well known forbidden transition having very low intensity (ϵ~15). The λmax 190 nm is due to π→π* transition with a better intensity (ϵ 10000).

Q.6 · Aqueous Soluti of Mecityl oxide shows two absorptions at 305 nm and 243 nm in its UV spectrum. Identify the UV spectrum. Which one is more intense and why?

Ans. The structure of mesityl oxide is 
$Me_2C=CH-C(=O)-Me$.

Two transitions occur (1) n→π* and (11) π→π*

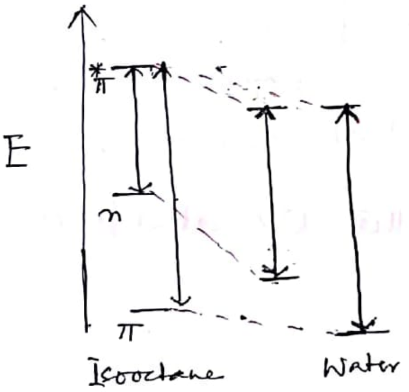
(1) n→π* transition occurs at 305 nm, and (11) π→π* occurs at 243 nm since the energy gap between n→π* < π→π*.
Of these two bands n→π* is least intense because it is a forbidden transition (the n and π* orbitals are mutually orthogonal to each other). π→π* is symmetry allowed hence appear as intense band.

Q.7. Mesityl oxide shows absorption bands at 230 nm and 321 nm in isooctane. Assign them in terms of electronic transition. How do these change if the solvent is changed to water? What change will you observe if similar solvent change is carried out in butadiene.?

Ans.

321 nm — $n \rightarrow \pi^*$ } in isooctane.
230 nm — $\pi \rightarrow \pi^*$ }

If water is used as solvent the $n \rightarrow \pi^*$ transition will ~~suffer~~ be shifted to lower wave length (blue shift) because the polar protic solvent water will stabilize the n orbital better than π^* through hydrogen bonding. The gap between the non bonding MO and π^* will increase and the solvent water on the other hand stabilise π^* MO more than π M.O (than when in isooctane). The energy gap between π and π^* decreases and hence $\pi \rightarrow \pi^*$ transition will occur at higher λ max value than 230 nm.



In case of butadiene there is only $\pi \rightarrow \pi^*$ transition. Now π^* being more polar than π orbital will be stabilised more by water (than isooctane). The $\pi \rightarrow \pi^*$ gap will thus decrease and a bathochromic shift is expected. But since both π and π^* orbitals of butadiene are practically non polar, no notable shift will be observed if such solvent change is done with butadiene.

Q8. Saturated aliphatic Ketones usually record three absorption maxima in UV spectrum at around 160 nm, 190 nm and 280 nm. Assign the transitions. Which one is most intense and why?

Q.9. What is end absorption? Why it is called so?

Q.10. Relate the λ_{max} values of (i) 277 nm & 185 nm and (ii) 324 nm & 219 nm to the compounds $CH_3-CO-CH_2-CH_3$ and $CH_3-CO-CH=CH_2$. Identify the electronic transitions.

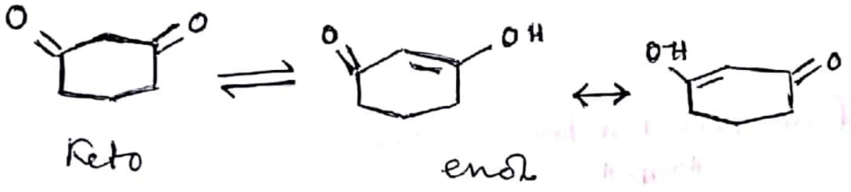
Ans. In the first compound two transitions occur, namely $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. The $n \rightarrow \pi^*$ requires less energy than $\pi \rightarrow \pi^*$ transition. Hence λ_{max} 277 nm is due to $n \rightarrow \pi^*$ and λ_{max} 185 nm is due to $\pi \rightarrow \pi^*$ transition; In the second compound the C=O gr is in conjugation with C=C moiety. Now the π and π^* orbitals of both C=O and C=C will ~~undergo~~ interact with each other and will decrease the energy gap between the HOMO & LUMO resulting in bathochromic shift of both the transitions. So $\pi \rightarrow \pi^*$ will absorb at 219 nm and $n \rightarrow \pi^*$ at 324 nm.

Q.11. Why it is difficult to measure the UV absorption of $\sigma \rightarrow \sigma^*$ transition?

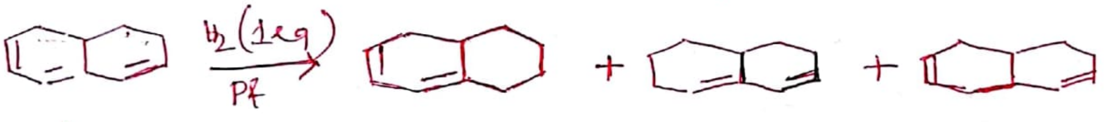
Ans. The $\sigma \rightarrow \sigma^*$ transition occurs near 150 nm. The transition below 200 nm are not generally considered, because below 200 nm O_2 in air begins to absorb and interfere with the other absorptions in this region. For $\sigma \rightarrow \sigma^*$ transition to measure a special technique is to be adopted. The whole path-length of the spectrophotometere must be evacuated – the region below 200 nm is called vacuum UV region.

Q.12. The UV absorption maxima of cyclohexa 1,3 di-one in ethanol shows a strong band at 253 nm (ϵ, 22000). Do you think that the intensity of this absorption (ϵ) will change significantly if the solvent is changed to H_2O or isooctane?

Ans. The enol tautomer of this cyclic enolisable β-diketone is unable to form intramolecular H-bond due to rigid transoid geometry of the enone. So both keto and enol form will be almost equally solvated if the solvent is changed from aprotic to protic or non polar to polar. So the equilibrium constant as well as the percentage of the absorbing species (enol form) remains practically unchanged in different solvents. There will be no significant change in intensity of the absorption with the change of solvent.



Q13. The triene 4 on partial hydrogenation gives three dienes 5, 6 & 7. How do you distinguish them from UV spectra?



4 5 6 7

Ans:

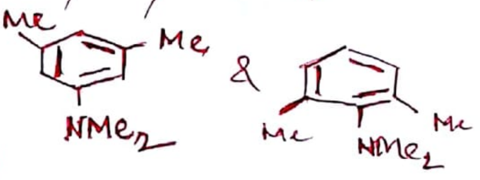
Q.14 How will you distinguish between the following pairs using UV-Spectroscopy?

(i) Phenol & 4 nitrophenol. (ii) Orthonitro aniline & P-nitro aniline.

(iii) 4-nitrophenol & 3,5 dimethyl 4 nitrophenol.

(iv) 4-hydroxy acetophenone & 4methoxyacetophenone.

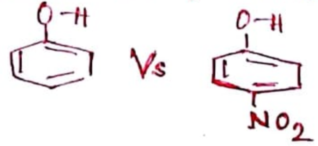
(v)



(vi) Cis & Trans Stilbene

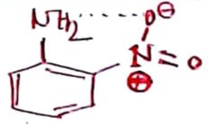
(vii)

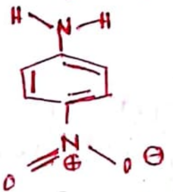
Phenol vs 4-nitrophenol.



The resonance hybrid of phenol contains three resonating structure and P-nitrophenol contains five resonating structures having negative charge on the less electronegative carbon atom and positive charge on more electronegative oxygen. Thus greater amount of conjugation decreases the gap between HOMO & LUMO and thereby ~~the~~ P-nitrophenol absorbs at a higher wavelength than that of phenol.

Orthonitroaniline and P-nitroaniline.





Orthonitroaniline possesses intramolecular hydrogen bonding but the p isomer has intermolecular hydrogen bonding. Intramolecular hydrogen bonding force increases the stability and thus decreases the energy content of the excited state than the intermolecular hydrogen bonding