

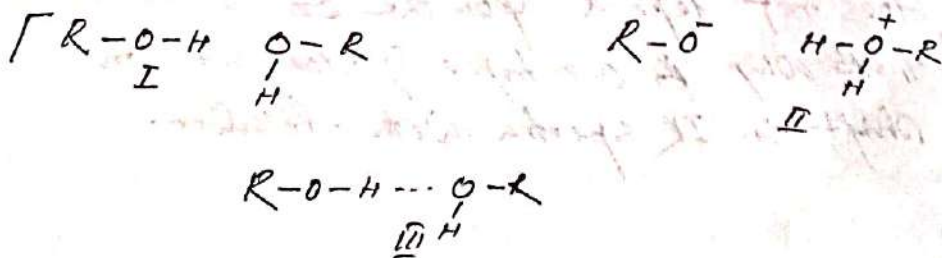
## IR-Spectra

\* How would you distinguish between intramolecular and intermolecular hydrogen bonding with the help of IR

Ans

Hydrogen bonding brings about remarkable downward frequency shift in IR spectra. Stronger the hydrogen bonding greater is the absorption shift towards lower wave number than the normal value. Two types of hydrogen bonds can be readily distinguished in infra-red technique. Generally, intermolecular hydrogen bonds give rise to broad bands whereas band arising from intramolecular hydrogen bonds are sharp and well defined. Intermolecular hydrogen bonds are concentration dependent. On dilution the intensities of such bands are independent of concentration. The absorption frequency difference between free and associated molecule is smaller in case of intramolecular hydrogen bonding than that in intermolecular association.

In aliphatic alcohols a sharp band appears at  $3650 \text{ cm}^{-1}$  in dilute sol<sup>n</sup> due to free O-H group while a broad band is noticed at  $3350 \text{ cm}^{-1}$  due to hydrogen bonded O-H group. Alcohols are strongly hydrogen bonded in condensed phases. These are usually associated as dimers and polymers which result in broadening of bands at lower absorption frequencies. In vapour state or in inert solvents, molecules exist in free state and absorb strongly at  $3650 \text{ cm}^{-1}$ . Alcohols can be written in the following resonating structures.



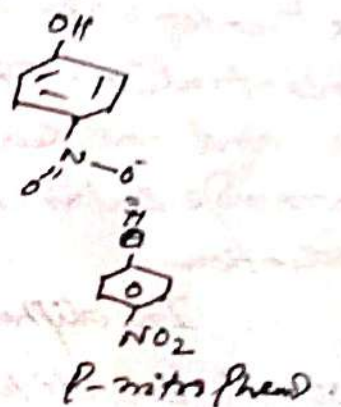
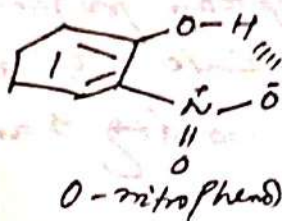
Structure III is the hybrid structure of I and II. This results in lengthening of the original O-H group. The

The electrostatic force of attraction between the oxygen atom of one molecule attracted by the oxygen atom of another molecule makes it easier to pull hydrogen away from oxygen atom. Thus small energy will be required to stretch such a bond and hence absorption occurs at a lower wave number.

\* How can you distinguish between o-nitrophenol and p-nitrophenol by IR Spectroscopy?

Ans

o-nitrophenol has intramolecular H-bonding between -OH and -NO<sub>2</sub> group, whereas p-nitrophenol possesses an intermolecular H-bonding between the above two groups with the help of another and another molecule.

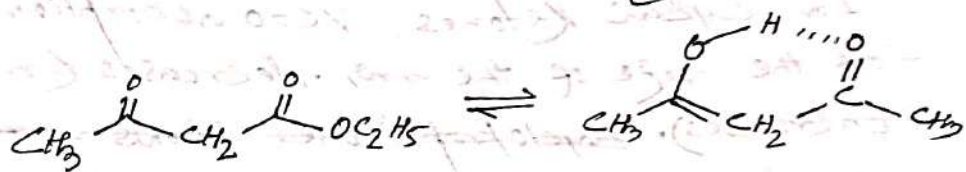


The above two can be easily distinguished by taking Infrared spectra of the given compound at two different concentrations. p-nitrophenol will ~~not~~ show a shift in the absorption position of -OH group with dilution but o-nitrophenol would not. Since intramolecular hydrogen bonding in a substance does not depend upon the concentration of solution, that's why p-nitrophenol does not show an absorption shift in IR spectra with dilution.

\* IR Spectra of ethyl acetoacetate shows absorption at 1733 ~~1784~~ cm<sup>-1</sup>, 1710 cm<sup>-1</sup> and 1650 cm<sup>-1</sup>. Explain.

Ans

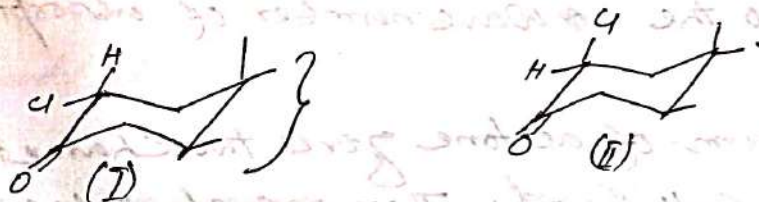
Keto esters like ethyl acetoacetate exhibit keto-enol tautomerism since they have ~~an~~  $\alpha$ -H atom. The infrared spectrum of the compound contains bands due to C=O, O-H and C=C ~~and~~ bonds. Ethyl acetoacetate exists in keto-enol isomer in equilibrium.



$\nu$  C=O str for ester - 1733 cm<sup>-1</sup>       $\nu$  C=O str 1645 cm<sup>-1</sup>  
 Carbonyl - 1710 cm<sup>-1</sup>

The lowering of  $\nu$  C=O str. absorption in the enolic form is due to intra-molecular hydrogen bonding which is stabilised by resonance.

\*



Compare  $\nu$  C=O stretching frequency of I and II

Ans:

The spectra of  $\alpha$ -halogenated cyclic ketones are particularly interesting in establishing the configuration of the halogen atom. In  $\alpha$ -halogeno-cyclohexanone, the equatorial halogen atom is practically eclipsed by the carbonyl group which has a trigonal geometry. If halogen atom is axial, then it must be in the staggered position relative to the carbonyl oxygen atom. In a conformation in which halogen atom is equatorial, the almost parallel dipole of C-X and C=O bonds result in the rise of  $\nu$  C=O absorption by 20 cm<sup>-1</sup> whereas no shift in the  $\nu$  C=O absorption is caused when halogen is in the axial position.

\* In IR spectroscopy, the bonded -OH structure appears at lower frequency than free -OH group.  
→ already discuss

\* Carbonyl IR band of cyclohexanone appears at 1705 cm<sup>-1</sup> while that of cyclopentanone at 1710 cm<sup>-1</sup>. Why?

Ans

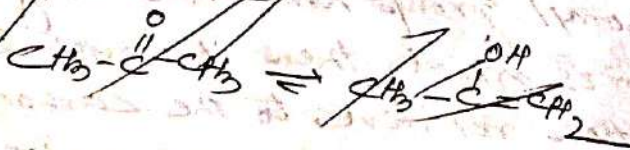
In cyclic ketones,  $\nu_{C=O}$  absorption increases as the size of the ring decreases (ring strain increases). ~~Cyclohexanone shows lower~~ A rise in  $\nu_{C=O}$  with decrease in ring size is due to the changes in the state of hybridisation in small rings. As the ring size decreases, the ring bonds become enriched in p-character and C=O bond acquires greater s-character. Hence force constant for C=O bond increases and also the wavenumber of absorption rises.

\* IR spectrum of acetone gives two characteristic bands for C-H bond. They are at 1360 cm<sup>-1</sup> and 3000 cm<sup>-1</sup> respectively. How do you describe it?

Ans

Acetone exists in equilibrium with their enolic form.

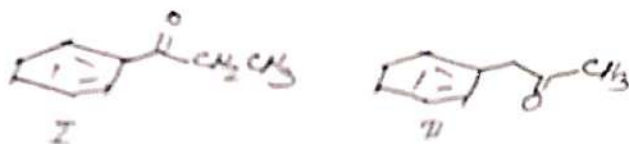
Acetone exist in equilibrium with their enolic form



The peak

The two peak at 3000 cm<sup>-1</sup> and 1360 cm<sup>-1</sup> are due to C-H stretching and C-H deformation absorptions

\* What would be the difference in their carbonyl absorption peaks in the IR spectra.

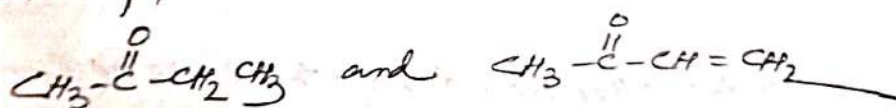


Ans

The  $\nu_{C=O}$  absorption for aryl ketone is lower than that in alkyl ketones. For arylalkyl ketones, the +I effect due to aryl group has an additional effect besides conjugation of C=O with the ring.  $\nu_{C=O}$  absorption for these compounds occur near about 1685-1690  $\text{cm}^{-1}$ . On the other hand compound like (II) mostly behave like an alkyl ketone since aromatic ring not directly attached to carbonyl group and it shows carbonyl absorption comparatively higher than compound (I).

\* Dilution has no effect on O-H stretching frequency of o-nitrophenol — Explain  
 → Already discuss

\* How will you distinguish the following pair of compound by IR spectroscopy



Ans: In the case of some electron withdrawing groups which also cause  $\alpha, \beta$ -unsaturation viz, alkenyl, alkynyl, aryl etc., the conjugative effect dominates over inductive effect and the result is net decrease in the wave number of carbonyl absorption. In the second compound conjugative effect dominates over -I effect and carbonyl absorption occurs at low wave number.

On the other hand in the case of compound (I) +I effect of two alkyl group decreases the carbonyl stretching frequency. Since conjugative effect more dominating than the +I effect, compound (II) will show lower

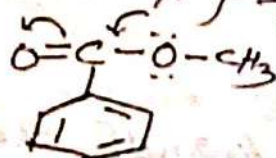
Carbonyl stretching frequency than (i). Compound (ii) will also show a C-O stretching frequency at 1625-1650 cm<sup>-1</sup> region.

\* How can you distinguish the following pairs of compound by IR spectroscopy?



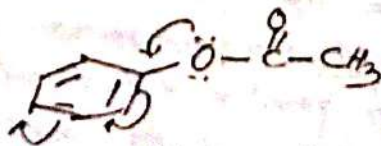
Ans

In case of compound (i), where the lone pair electrons present on an oxygen is in conjugation with the double bond of carbonyl group the mobility of the electron matters. Due to the conjugation of lone pair in the C=O group, carbonyl stretching frequency decreases compared to normal carbonyl frequency.



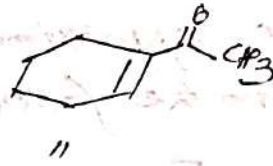
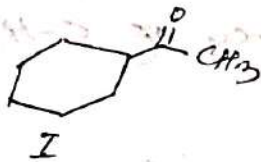
$\nu_{C=O}$  1730 cm<sup>-1</sup>

On the other hand in the case of compound (ii), inductive effect dominates over mesomeric effect and hence absorption takes place at comparatively higher frequencies.



$\nu_{C=O}$  1770 cm<sup>-1</sup>

So we can distinguish the two compounds with the help of carbonyl stretching frequency.



Ans

In the case of compound (II) mesomeric effect causes lengthening or the weakening of a bond leading in the lowering of carbonyl absorption frequency compared to compound (I) where such type of effect is absent.

\* Why is the finger print region in IR-spectroscopy so important?

One of the important functions of Infrared Spectroscopy is to determine the identity of two compounds. Two identical compounds have exactly the same spectra when run in the same medium under similar conditions. The region below 1500 cm<sup>-1</sup> is rich in many absorptions which are caused by bending vibrations and those resulting from the stretching vibrations of C-C and C-O and C-N bonds. In a spectrum the number of bending vibration is usually more than number of stretching vibrations. The said region is usually rich in absorption bands and shoulders. It is called Finger print region. Some molecules containing the same functional group show similar absorption above 1500 cm<sup>-1</sup> but their spectra differ in finger print region. Thus this region is different for every individual compound ~~and~~ except the enantiomers. Thus we can distinguish the two different compound by compared their finger print region.

Q. Calculate the approximate frequency of C-H stretching vibration from the following data:

$$\text{Force constant (K)} = 5 \times 10^5 \text{ gm/sec}^2$$

$$\text{Mass of Carbon atom} = 20 \times 10^{-24} \text{ gm}$$

$$\text{Mass of Hydrogen atom} = 1.6 \times 10^{-24} \text{ gm}$$

Ans.

We know that fundamental vibrational frequency is expressed as

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

$$K = 5 \times 10^5 \text{ gm/sec}^2$$

$$\text{Reduced mass} = \mu_{\text{C-H}} = \frac{m_{\text{C}} \times m_{\text{H}}}{m_{\text{C}} + m_{\text{H}}}$$

$$= \frac{20 \times 10^{-24} \times 1.6 \times 10^{-24}}{20 \times 10^{-24} + 1.6 \times 10^{-24}}$$

$$= \frac{(20 \times 1.6) \times 10^{-24}}{21.6}$$

$$= 1.48 \times 10^{-24} \text{ gm}$$

$$\therefore \bar{\nu} = \frac{1}{2 \times 3.14 \times 3 \times 10^{10}} \sqrt{\frac{5 \times 10^5}{1.48 \times 10^{-24}}}$$

$$= \frac{1}{2 \times 3.14 \times 3 \times 10^{10}} \sqrt{3.37 \times 10^{29}}$$

$$= 0.053 \times 10^{10} \times 10^{14} \sqrt{30.37}$$

$$= 0.053 \times 5.51 \times 10^4$$

$$= 0.29203 \times 10^4$$

$$= 2920.3 \text{ cm}^{-1}$$

✓