Infrared Study of Keto-Enol Equilibrium of Acetylacetone, Benzoylacetone and Dibenzoylmethane in Various Organic Solvents

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Summary: The keto-enol equilibrium of acetylacetone, benzoylacetone and dibenzoylmethane in various polar and non-polar solvents have been calculated using IR technique. Substitution of methyl group by phenyl group in acetylacetone shifts the equilibrium towards the enol form due to increase of resonance energy of the enol form and therefore dibenzoylmethane is completely enolized, the enol content increases as the polarity of the solvent decreases. The band at 1695 cm^{-1} in the spectrum of acetylacetone relatively varies with solute concentration in non-polar solvent. This band attributes to the presence of small amount of non-chelated enol molecules which are absent in the other two compounds.

Introduction

Keto - enol quilibrium can be investigated by many physical and chemical methods [1-11]. However it has been shown that spectroscopic methods are the most powerful tools in the study of the equilibrium because spectroscopic measurements do not interrupt the equilibrium state. However, infrared and N.M.R. techniques have been shown to be more sensitive than U.V. for studying the tautomeric mixture [7,8,12,13,14]. 1,3 Diketones such as acetylacetone, benzoylacetone and dibenzoylmethane, etc. undergo tautomerization and exist mainly in the chelated mono-enolic form in non-polar solvents such as carbon tetrachloride [1-3].

Raman spectra of many diketones were studied by Kohlraush[2] and Shigorin and Sheverdina [15,16,17].

The infrared spectra of acetylacetone dibenzoylmethane and benzoylacetone have been already reported by many investigators: Rasmussen et al. [3], Smith [18] Ballamy and Beecher [19], and Bratoz et al. [20].

Rasmussen et al. [3] were interested mainly in the $\nu(OH)$ and $\nu(C=O)$ bands and discussed the influence of chelation on their position, whereas Bratoz et al.[20] were interested in the location of the bands controlled by the vibration of the O-H group. Ogoshi and Nakamoto [21] have carried out an intensive study of infrared spectra of the enol forms of acetylacetone and hexafluoroacetylacetone and their deutro analogs in the region 4000-700 cm^{-1}. They have carried out normal coordinate analysis to estimate the force constants as well as to make theoretical bands assignments, they were also interested in the effect of substituents on the chelate ring.

Burdett and Rogers have shown that under the same conditions, the enol form is more predominant in hexafluoro acetyl acetone than in acetyl-

acetone [22]. The aim of the present work was to investigate the solvent effect on enol-keto equilibrium of acetylacetone, benzoylacetone and dibenzoylmethane using infrared technique.

Experimental

A. Chemical and Spectral Measurements

Most of the substances used in this work were commercial samples of analar grade and no further purification was made.

The spectra were recorded with a Unicam infrared spectrophotometer model SP-1100, equipped with a rock-salt prism and in all measurements NaCl cell with path length 0.1 mm was used.

The measurements were carried out at room temperature and in each solvent at least five concentrations were used.

B. Procedure of Calculations

Spectra of acetone and acetophenone at various concentrations in the interested solvents were measured. These measurements have shown that the intensity and position of C=O group frequency of the two compounds are not remarkably affected by the solvents [3] therefore the calculations of the equilibrium were based on the determination of keto form concentration in each solvent using the C=O molar absorptivities of acetone and acetophenone in the corresponding solvent. The concentration of the keto form at infinite dilution was obtained by extrapolation.

Results and Discussion

The IR spectrum of acetylacetone in CCl_4 shows two bands in the double bond region (fig.1) as a strong and broad band at 1610 cm^{-1} and a weak doublet band near 1720 cm^{-1}. The band at 1610 cm^{-1} is interpreted as super position of the C=O streching and C=C streching coupled with C-H in plane bending of the enol form [21] whereas the weak band at 1720 cm^{-1} is attributed to C=O stretching of the keto form. The large lowering in the C=O frequency of the enol form indicates that enol is present as conjugate chelated system [3]. The high intensity of this band leads to the suggestion that over 90% of acetylacetone is enolized when dissolved in non-polar solvents. On the other hand benzoylacetone spectrum (fig.3) shows three bands in the double band region: 1715 cm^{-1}, 1695 cm^{-1} and 1603 cm^{-1}. The former weak band can be attributed to the keto form whereas the latter band is assigned to C=O of the enol form. The two bands at 1715 cm^{-1} and 1695 cm^{-1} are interpreted as C=O stretching of the carbonyl group attached to methyl and pehnyl groups respectively.

The IR spectrum of dibenzoylmethane (fig.4) exhibits one strong broad band in the double bond region at 1605 cm^{-1} and no band due to free carbonyl being noted; presumably this compound is completely present in the mono-enolic form. This band can be interpreted as superposition of C=O stretching and C=C stretching coupled with C-H bending and stretching of the benzene ring of the enol form.

Turning again to acetylacetone the carbonyl groups of the keto form are identical and therefore expected to show only one band near 1720 cm^{-1} Therefore the band at 1695 cm^{-1} could be assigned to stretching of non hydrogen bonded conjugated carbonyl group because it lies in the usual
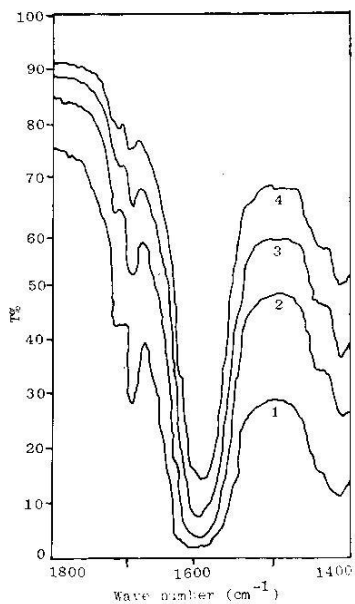
Fig.1 Spectra of acetylacetone in CCl_4 in the double bond region at various concentrations decreasing 1 to 4; 1) 0.8660 2) 0.5022 3) 0.3716 4) 0.2601 M in 0.1 mm cell.
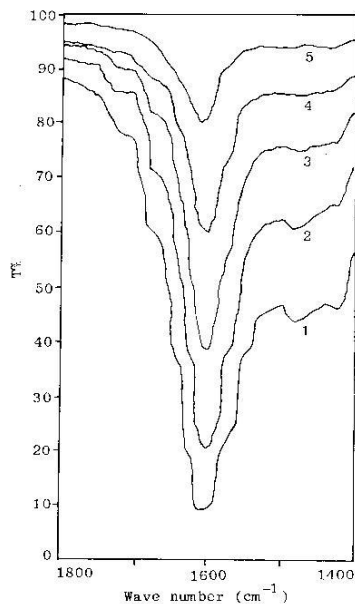

Fig.3 Spectra of benzoylacetone in CCl_4 in the double bond region at various concentrations decreaing 1 to 5 . 1)0.2765 2) 0.1658 3) 0.0995 4) 0.0597 5) 0.0238 M in 0.1 mm cell.
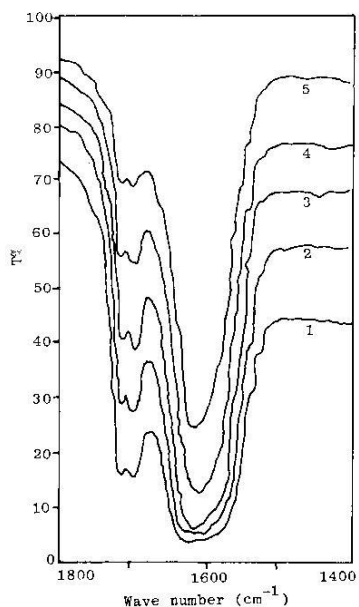

Fig.2 Spectra of acetylacetone in ethanol in the double bond region at various concentrations decreasing 1 to 5 ; 1) 1.2030 2) 0.7940 3) 0.5878 4) 0.3878 5) 0.2482 M in 0.1 mm cell.
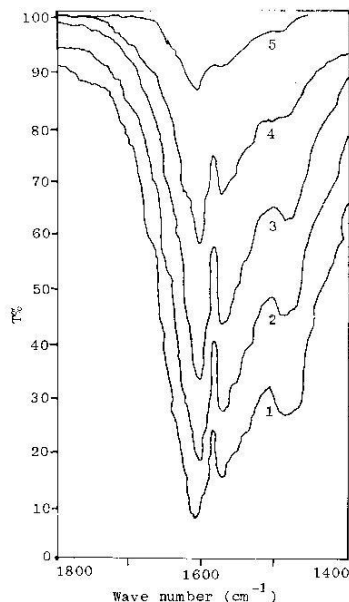

Fig.4 Spectra of dibenzoylmethane in CCl_4 in the double bond region at various concentrations decreasing 1 to 5 ; 1) 0.2232 2) 0.1339 3) 0.0857 4) 0.0342 5) 0.0137 M in 0.1 mm cell.

conjugated ketone region [3]. This indicates the presence of a small quantity of trans molecules.

However the mono-enolic non-chelated form is relatively small. This point is strongly supported by the fact that IR spectrum of acetylacetone in the O-H stretching frequency region shows a weak band at 3560 cm^{-1} which is absent in the spectra of the two other compounds. The fact that no bands in the usual conjugated ketone region in the spectra of both dibenzoyl methane and benzoylacetone are observed leads to the suggestion that no molecules of these compounds are present in trans forms. This is expected since the large spatial demand of benzene ring destabilizes all the conformations of the keto form and accordingly the keto-enol equilibrium shifts towards the enol.

The main feature of the spectra of the three compounds is the lack of absorption near 3350 cm^{-1} where simple hydrogen bonded O-H absorption occurs, and the weak band near 2700 cm^{-1}, an unusual absorption position, therefore this band accounts for the O-H vibration which is extremely broadened in an analogous way to the fatty acid dimer [23]

The other feature of interest in the spectrum of acetylacetone (fig.1) is the variation of the relative intensities of the two bands, 1720 cm^{-1} and 1695 cm^{-1} with concentration in non-polar solvents such as CCl_4.

The intensity of 1695 cm^{-1} band relatively decreases as the concentration decreases, whereas in polar solvent such as ethanol it is not effected, this could be understood on the following basis. Acetylacetone is more polar than CCl_4 and at high concentration, acetylacetone can be imagined to serve as solvent. Since the band at 1695 cm^{-1} measures the non-chelated enolic form which is more polar than the keto form, the equilibrium between keto and non- chelated enol form is relatively shifted to the latter at high concentration, whereas in ethanol (fig.4) which is more polar than keto and non-chelated enolic forms the equilibrium is expected to be not much effected by variation of concentration, although the total enolized form is less than that in CCl_4.

It is well known that many factors have pronounced effect on the keto-enol equilibrium, such as H-bonding, resonance, steric entropy and solvation.

Table (1) shows that in non-polar solvents dibenzoylmethane is completely enolized; however benzoylacetone is more enolized than acetylacetone. This is due to the fact that the substitution effect of phenyl group increases the resonance energy of the keto as well as the enol tautomer but much more for the latter. On the other hand the bulkiness of the phenyl group destabilizes all the conformation of the keto form.
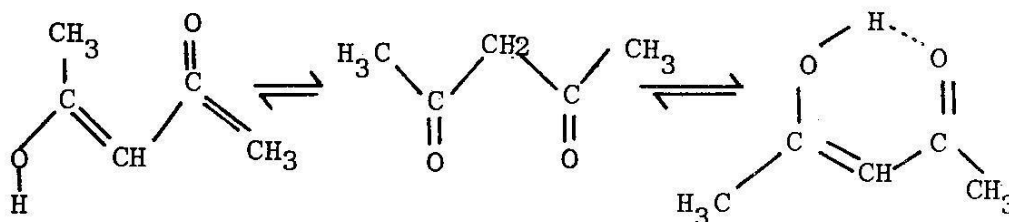
Table-1: Enol content and equilibrium constant (Ke) in various solvents

1,3-Diketone	Percent enol	Ke	Solvent
$CH_3COCH_2COCH_3$	91.2	10.36	n-hexane
	82.8	4.78	carbon tetrachloride
	74.0	2.84	chloroform
	77.9	3.51	benzene
	70.7	2.40	ethanol
	57.0	1.32	1,4-dioxane
$C_6H_5COCH_2COCH_3$	98.2	54.40	n-hexane
	93.0	13.30	carbon tetrachloride
	70.0	2.33	chloroform
	92.5	13.10	diethylether
	81.5	4.40	1,4-dioxane
	72.0	2.57	methanol
	67.0	2.03	ethanol
$C_6H_5COCH_2COC_6H_5$	100		carbon tetrachloride
	not sufficiently soluble		n-hexane
	100		chloroform
	100		1,4-dioxane
	98.2	54.4	diethylether
	not sufficienty soluble		methanol

It is clear from the data in table (1) that enol content decreases as the solvent polarity increases [12]. This observation can be explained as follows. Although the ionic forms contribute to the resonance structures of the enol it is less polar than the ketone because of the intrahydrogen bond in the enol. Therefore polar solvents should stabilize the keto forms and the enol content should be higher in non-polar solvents. On the other hand hydroxylic solvents such as ethanol would form H-bonds with solute oxygen atom to compete with the intramolecular H-bond in the enol leading to decrease in the enol content.

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