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by

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Spectrophotometric Studies on Some 3-phenyl-3-pxo propionitriles: An Insight To The Structure and Acid-Base Characteristics.

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ABSTRACT

The ionization constants of some substituted 3-phenyl-3-oxo-propionitrile are determined spectrophotometrically, the results indicate the existence of two ionization steps corresponding to the ionization of two protons of the CH_2 group. The effect of substituents on pK values is investigated. The infrared spectra are recorded and the most important bands were discussed.

INTRODUCTION

3-oxopropionitrilis (I) are versatile synthons for a variety of organic compounds. The exceptional reactivity of this class of compounds is apparently due to the methylene group in position 2 being adjacent

$$R-\overset{\overset{O}{\|}}{C}-CH_2-CN$$

(I)

to keto and cyano functions. Consequently tautomeric structures like (II) and (III) were reported[1,2].

$$\underset{(I)}{R-\overset{\overset{O}{\|}}{C}-CH_2-CN} \leftrightarrow \underset{(II)}{R-\overset{\overset{OH}{|}}{C}=CH-CN} \leftrightarrow \underset{(III)}{R-\overset{\overset{O}{\|}}{C}-CH=C=NH}$$

Arndt et al[3] have shown that 3-phenyl-3-keto-propionitrile ($R=C_6H_5$) exists mainly as trans-3-hydroxy cinnamonitrile. Some authors[2,4,5] have presented physical data in favour of this view. On the other hand 2-substituted-3-keto-nitriles were found to exist mainly in the keto form (I)[2,6,7,8]. Generally, the reported articles were concerned mainly with the tautomeric forms with no emphasize about the acid-base equilibria possibly displayed by these compcunds.

This article is therefore intended to investigate the reactivity of this class of compounds from this point of view based on spectral data (ir) and (UV) in buffer solutions of different pH values. Meanwhile the work was extended to investigate whether a linear free energy relationship applies via inspection of the effect of substituents.

EXPERIMENTAL

Organic Syntheses:

3-phenyl-3-oxo-propionitriles were prepared as previously described by Obregia[9] and Cabreil[10] through the reaction of phenacyl bromide (or the corresponding substituted phenacyl bromide) with KCN in aqueous ethanol in the presence of basic catalyst. The crude product was recrystalized from ethanol and the purity credit was checked by TLC and standard microanalytical elemental analysis.

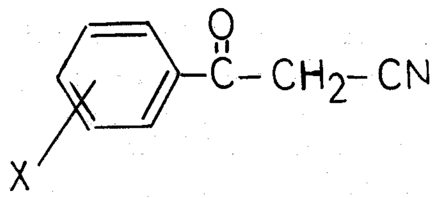
The absorption spectra were recorded in the uv-region in 40 % ethanolic Britton-Robinson buffers[11] using PYE UNICAM SP 1800 recording spectrophotometer. A certain volume of 10^{-3} M solution was completed with the required buffer in 25 ml measuring flask. The pH values of the solutions were checked after scanning the absorption spectra by the aid of a digital pH-meter, type Minisis 5000-Solea Tacussel (France).

The ir spectra were recorded using the KBr disc technique with the aid of PYE UNICAM SP 2000 infrared spectrophotometer.

The pK values were calculated from the variation of absorbance with change of pH values applying the half height and limiting logarithmic methods[12].

RESULTS AND DISCUSSION

The 3-oxonitriles prepared for this investigation have the general structural formula:



I

X = H (a), p-OCH_3(b), p-CH_3(c), m-CH_3(d), p-NH_2(e), p-Br (f) and m-NO_2(g).

1- UV Spectra:

The absorption spectra of the seven 3-oxonitriles were studied in 40 % ethanolic buffers covering the pH range 2-12. In acid media the spectra displayed a sharp band in the region 270-290 nm and a shoulder at 295, 285 and 305 for $I_{b,d}$and e. This band is broadend and shifted to longer wavelength in alkaline media for all compounds except for $I_a$and e where the shift is to shorter wavelength. The values of λ_{max} of this band in acid, basic and in pure alcohol media are listed in table 1. This band may be assigned to $\pi-\pi^*$electronic transition influenced by charge transfer interaction. Further support for this assumption could be obtained by calculating the energy of the charge transfer (CT) interaction using the relation[13]:

Table (1)

λ_{max} of 3-oxonitriles in different media

No	X	max, nm					
		Ethanol		acidic media		alkaline media	
I_a	H	280		277		290	
b	p–OCH_3	275 sh,	293	280,	295 sh	282,	293
c	p–CH_3	272		272		295 vb	
d	m–CH_3	279,	287 sh	280,	285 sh	275,	283
e	p–NH_2	284,	300 sh	288,	305 sh	280,	305
f	p–Br	272,	281	274		275,	300 b
g	m–NO_2	273		274		274	

sh = shoulder, vb = very broad, b = broad.

$$ECT = I_p - (E_f + C)$$

where, I_p: the ionization potential (taken as that of benzene 8.95 ev)[14]

E_f: the electron affinity of the C=0 group (-1.35 ev)[15] and,

C: is the coulombic force between the electron transferred and the positive hole left behind.

The calculated value 4.60 ev for I_a is in agreement with the experimental value 4.43 ev.

The absorption band is subjected to pronounced changes in both position and absorbance values on changing pH value of the medium. In alkaline solution the band is shifted to longer wavelength where a very broad band appears in compounds I_{a-c} (cf. Fig. 1), while in compo-

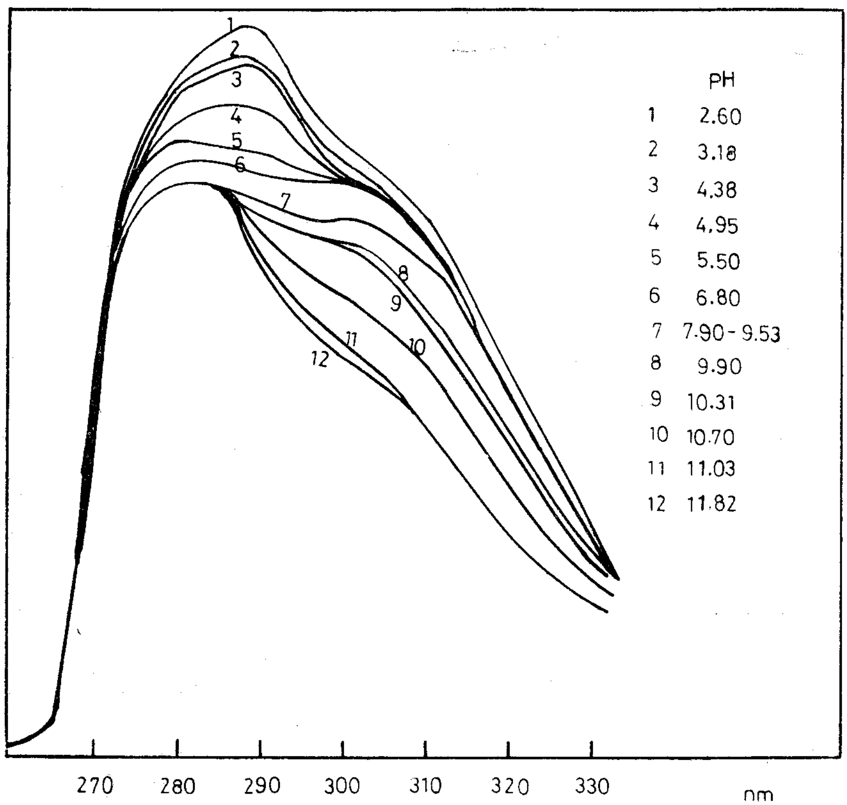


Fig. 1: Electronic absorption spectra of $2.5x10^{-4}$ M (I_e) in 40 % by volume ethanolic Britton Robinson buffers.

unds I_f and g only changes in absorbance are observed (table 1). This red shift may be attributed to the formation of the negatively charged species in alkaline media thus facilitating the charge transfer interaction leading to higher conjugation within the molecule.

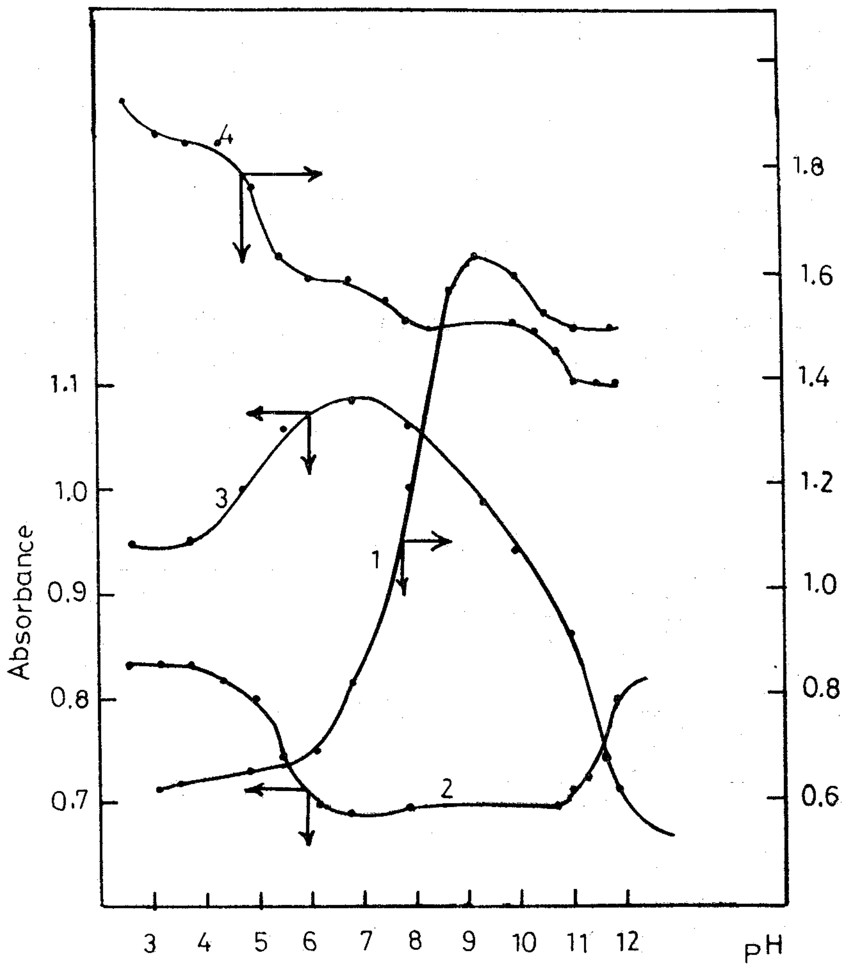
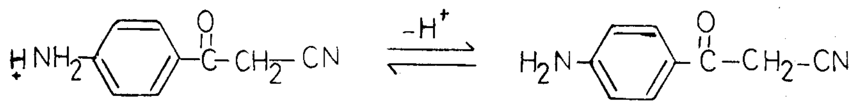


Fig (2)

Fig. 2: Absorbance-pH curves for (I_a) at 290 nm. (1), (I_d) at 280 nm (2); (I_c) at 300 nm (3); (I_e) at 290 nm (4).

The absorbance-pH curves at different wavelengths (Fig. 2) exhibit mostly two steps at two different regions. This may be taken as evidence that these compounds exhibit two ionization steps (except I_b and e) where only one infletion is observed for the first while three inflections were observed for the second which may be accounted by the presence of another ionization step for the quarternary salt, thus:

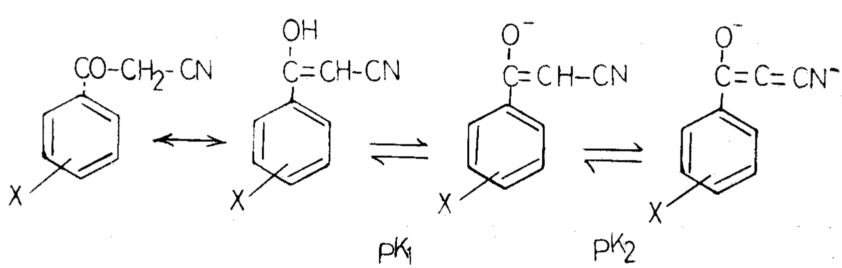


The variation of absorbance whit change of pH of the medium was utilized for calculating the ionization constant values following using previously reported procedures[12]. The calculated values are listed in Table 2. The ionization may be represented as:

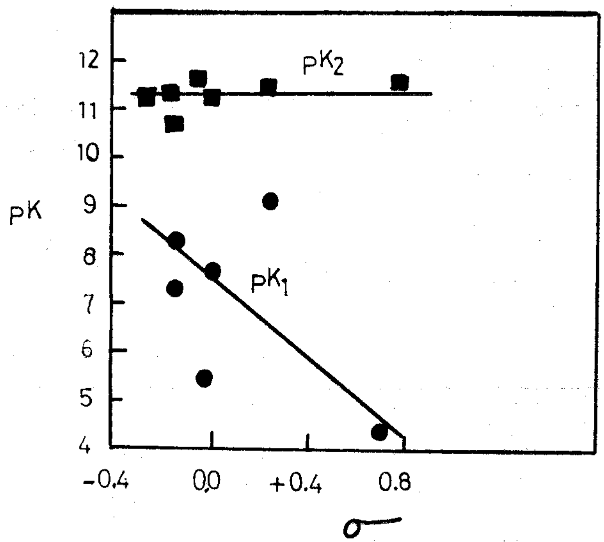
Table (2)
pK values of 3-oxinitriles

	X	σ	pK values[a]		
I_a	H	—0.00		7.70	10.20
b	p-OCH_3	—0.26		—	11.25
c	p-CH_3	—0.17		8.25	11.30
d	m-CH_3	—0.067		5.40	11.60
e	p-NH_2	-0.16	5.10[b]	7.25	10.70
f	p-Br	+0.23		9.10	11.50
g	m-NO_2	+0.71		4.40	11.60

a, mean pK b deprotonation constant



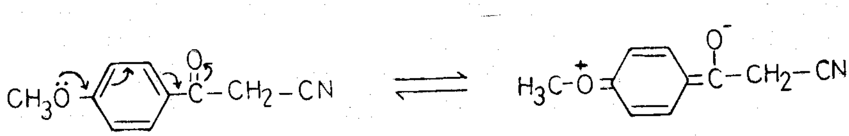
The validity of linear free energy relationship was tested by plotting pK values against σ –Hammett constant (cf. Fig. 3).



Fig(3)

Fig. 3: pK-Hammett's constantσ cotrelation for compounds I_{a-g}.

For pK_1 a straight line is obtained (ρ= 2.68, r = 0.51) indicating that the electron withdrawing groups increase the acidity of the parent compound whereas electron donating groups decreases the acidity and even for strong electron donating groups like p-OCH_3 such ionization could not be traced due to the participation of the quininoid structure IV (as a result of the CT) thus:



IV

For the second ionization step no significant effect of substituents was observed which may be interpreted by the fact that the species undergoing ionization are mainly the ketemine form (III) in which the ionizable centre is isolated from the substituted phenyl moiety.

2- ir-Spectra:

The main bands in the ir-spectra of the 3-oxonitriles under investigation are those of the CH, CO, CN groups. Table 3 summarizes the main bands of the ir spectra of compounds I_{a-g}.

Table (3)
Main bands in the ir-spectra of 3-oxonitriles

No X	Wavenumber, $\bar{\nu}$ cm^{-1}				
	C-0	C=0	C≡N	λCHsym	λCHassy
I_a H	1219	1693	2272	2932	2960
b p-OCH_3	1227	1688	2275	2930	2955
c p-CH_3	1248	1692	2265	2930	2960
d m-CH_3	1250	1695	2265	2932	2960
e p-NH_2	1228	1688	2282	2940	2968
f p-Br	1220	1690	2280	2938	2963
g m-NO_2	1218	1910	2280	2932	2960

Legends to Figures

The spectra of all compounds display the bands characteristic of aliphatic C-H stretching vibrations within the 2970-2930 cm^{-1} region. The 2970 cm^{-1} band is assigned to ν_{CH} sym. while the band around 2930 cm^{-1} is assigned to ν_{CH} assym.

The vibrations of the C=0 group leads to two bands, the first one within the range 1220-1250 cm^{-1} corresponds to the stretching vibration of the C-0 system, i.e. the carbonyl group in the polarized state. The appearance of this band supports the occurence of the intramolecular charge transfer leading to the formation of a carbon-oxygen single bond. The second band, lying within the 1688-1710 cm^{-1} range is assigned to the C=0 stretching vibration, i.e. in its ground state. The The position of the C=0 band denotes that the group would be involved in the keto-enol tautomerism with the neighbouring CH_2-group. The band shifts to higher wavenumbers on increasing the electron attracting character of the substituents indicating that the π-electrons on the

C=0 bond tends to be more localized. Thus the intramolecular charge transfer from the aromatic to the C=0 group becomes less affected.

A medium to low intensity band is observed within the range 2265-2280 cm^{-1}which can be assigned to the C=N stretching vibration. The low value of this band compared to alkyl nitriles can be explained by the participation of the group in a tautomeric shift with CH_2-group leading to structure (III).

The plots and statistical treatment using the least square method[16] of $\bar{\nu}$ values for the main ir-bands (cf. Fig. 4) show that only the C-0 band correlates fairly with the σ-Hammett constant (ρ = 19.5, r= 0.75) indicating the direct interaction between the C=0 group and the substituents. For the other bands no good correlation was obtained.

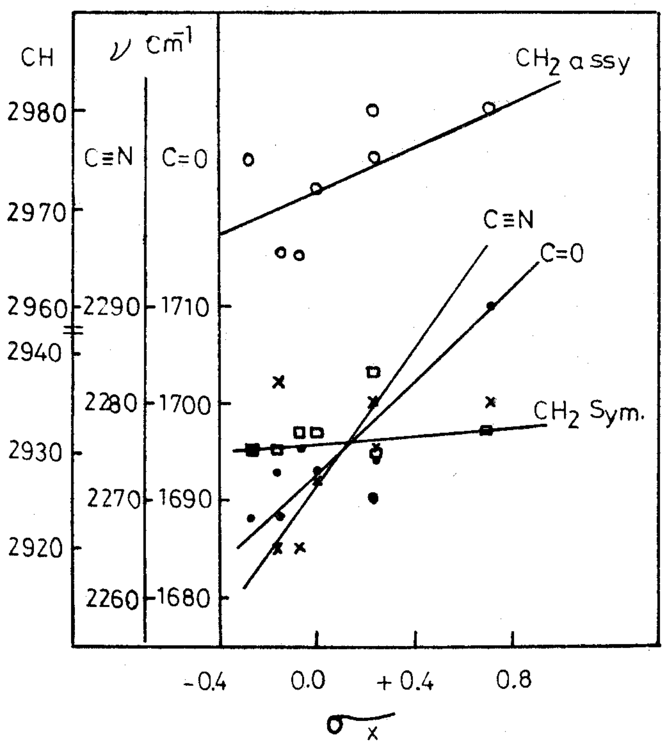


Fig (4)

Fig. 4: Wavenumbers-Hammett's constantσ correlation for the main bands of compounds I_{a-g}.

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