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

by

A.M.A. HILMY A.L. EL-ANSARY, M.A. MORSI,
La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les disciplines scientifiques représentées à la Faculté des Sciences de l'Université d'Ankara.

La Revue, jusqu'à 1975 à l'exception des tomes I, II, III était composé de trois séries

Série A: Mathématiques, Physique et Astronomie,
Série B: Chimie,
Série C: Sciences Naturelles.

A partir de 1975 la Revue comprend sept séries:

Série A₁: Mathématiques,
Série A₂: Physique,
Série A₃: Astronomie,
Série B: Chimie,
Série C₁: Géologie,
Série C₂: Botanique,
Série C₃: Zoologie.

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté des Sciences de l'Université d'Ankara. Elle accepte cependant, dans la mesure de la place disponible, les communications des auteurs étrangers. Les langues Allemande, Anglaise et Française seront acceptées indifféremment. Tout article doit être accompagné d'un résumé.

Les articles soumis pour publications doivent être remis en trois exemplaires dactylographiés et ne pas dépasser 25 pages des Communications, les dessins et figures portés sur les feuilles séparées devant pouvoir être reproduits sans modifications.

Les auteurs reçoivent 25 extraits sans couverture.

l'Adresse : Dergi Yayın Sekreteri,
Ankara Üniversitesi,
Fen Fakültesi,
Beşevler–Ankara
Spectrophotometric Studies on Some 3-phenyl-3-oxo propionitriles: An Insight To The Structure and Acid-Base Characteristics.

A.M.A. HILMY A.L. EL-ANSARY,* M.A. MORSI,

Chemistry Department, Faculty of Science, Elmansoura University and *Cairo University – Egypt.

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-oxopropionitrilies (I) are versatile synths 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

\[
R - \| - \text{CH}_2 - \text{CN}
\]

(I)

to keto and cyano functions. Consequently tautomeric structures like (II) and (III) were reported.$^{12}$

\[
\begin{align*}
0 & \quad \text{OH} & 0 \\
R - \| - \text{CH}_2 - \text{CN} & \longleftrightarrow R - C = \text{CH} - \text{CN} & \longleftrightarrow R - C - \text{CH} = \text{C} = \text{NH} \\
(\text{I}) & \quad (\text{II}) & \quad (\text{III})
\end{align*}
\]

Arndt et al$^{3}$ have shown that 3-phenyl-3-keto-propionitrile (R=C$_6$H$_5$) exists mainly as trans-3-hydroxy cinnamoni trile. 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 \( \text{I}^2,6,7,8 \). Generally, the reported articles were concerned mainly with the tautomeric forms with no emphasize about the acid-base equilibria possibly displayed by these compounds.

This article is therefore intended to investigate the reactivity of this class of compounds from this point of view based on spectral data \( \text{(ir)} \) and \( \text{(UV)} \) in buffer solutions of different \( \text{pH} \) 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 recrystallized 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 \( 10^{-3} \text{M} \) solution was completed with the required buffer in 25 ml measuring flask. The \( \text{pH} \) values of the solutions were checked after scanning the absorption spectra by the aid of a digital \( \text{pH} \)-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 \( \text{pK} \) values were calculated from the variation of absorbance with change of \( \text{pH} \) 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:
X = H (a), p-OCH₃(b), p-CH₃(c), m-CH₃(d), p-NH₂(e), p-Br (f) and m-NO₂(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 I₉a(d) and e. This band is broadened and shifted to longer wavelength in alkaline media for all compounds except for I₉a and e where the shift is to shorter wavelength. The values of $\lambda_{\text{max}}$ 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:

$$\text{Table 1}

\begin{array}{|c|c|c|c|}
\hline
\text{No} & \text{X} & \text{Ethanol} & \text{acidic media} & \text{alkaline media} \\
\hline
1 & \text{H} & 280 & 277 & 290 \\
2 & \text{p-OCH₃} & 275 \text{ sh}, 253 & 280, 295 \text{ sh} & 282, 293 \\
3 & \text{p-CH₃} & 272 & 272 & 295 \text{ vb} \\
4 & \text{m-CH₃} & 279, 287 \text{ sh} & 280, 285 \text{ sh} & 275, 283 \\
5 & \text{p-NH₂} & 284, 300 \text{ sh} & 288, 305 \text{ sh} & 280, 305 \\
6 & \text{p-Br} & 272, 281 & 274 & 275, 300 \text{ b} \\
7 & \text{m-NO₂} & 273 & 274 & \\
\hline
\end{array}

\text{sh = shoulder, vb = very broad, b = broad.}
ECT = $I_p - (E_r + C)$

where, $I_p$: the ionization potential (taken as that of benzene 8.95 ev)$^{14}$

$E_r$: 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 $I_d$ 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 Ia-e (cf. Fig. 1), while in compo-

Fig. 1: Electronic absorption spectra of 2.5x10^{-4} M ($I_p$) in 40 % by volume ethanolic Britton Robinson buffers.
unds I₄ 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: Absorbance-pH curves for (I₉) at 290 nm, (I₄) at 280 nm (2); (I₆) at 300 nm (3); (I₈) 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 I₄ and e) where only one inflection 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 quaternary salt, thus:

\[
\text{H}_{2}N\text{C}_{6}\text{H}_{4}\text{C}-\text{CH}_{2}-\text{CN} \quad \xrightleftharpoons{-\text{H}^{+}} \quad \text{H}_{2}N\text{C}_{6}\text{H}_{4}\text{C}-\text{CH}_{2}-\text{CN}
\]

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

Table (2)

<table>
<thead>
<tr>
<th>X</th>
<th>σ</th>
<th>pK values\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1ₐ</td>
<td>H</td>
<td>7.70</td>
</tr>
<tr>
<td>b</td>
<td>p-OC₃H₃</td>
<td>8.25</td>
</tr>
<tr>
<td>c</td>
<td>p-CH₃</td>
<td>7.40</td>
</tr>
<tr>
<td>d</td>
<td>m-CH₃</td>
<td>5.10\textsuperscript{b}</td>
</tr>
<tr>
<td>e</td>
<td>p-NH₂</td>
<td>9.10</td>
</tr>
<tr>
<td>f</td>
<td>p-Br</td>
<td>4.40</td>
</tr>
<tr>
<td>g</td>
<td>m-NO₂</td>
<td>6.50</td>
</tr>
</tbody>
</table>

\textsuperscript{a} mean pK  \textsuperscript{b} deprotonation constant
The validity of linear free energy relationship was tested by plotting pK values against σ-Hammett constant (cf. Fig. 3).

![Graph]

*Fig. 3: pK-Hammett’s constant correlation for compounds 1a-g.*

For pK₁ 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-OCH₃ such ionization could not be traced due to the participation of the quinonoid structure IV (as a result of the CT) thus:

\[
\text{CH}_3\text{O} = \text{C} - \text{CH}_2 - \text{CN} \quad \longleftrightarrow \quad \text{H}_3\text{C}^+ = \text{C} = \text{CH}_2 - \text{CN} \quad \text{IV}
\]
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 ketamine 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 Ia–g.

<table>
<thead>
<tr>
<th>No</th>
<th>X</th>
<th>C=O</th>
<th>C≡N</th>
<th>λ(CH sym)</th>
<th>λ(CH assy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>H</td>
<td>1219</td>
<td>1693</td>
<td>2272</td>
<td>2532</td>
</tr>
<tr>
<td>b</td>
<td>p-CH₃</td>
<td>1227</td>
<td>1688</td>
<td>2275</td>
<td>2930</td>
</tr>
<tr>
<td>c</td>
<td>m-CH₃</td>
<td>1248</td>
<td>1692</td>
<td>2365</td>
<td>2930</td>
</tr>
<tr>
<td>d</td>
<td>m-NH₂</td>
<td>1250</td>
<td>1695</td>
<td>2265</td>
<td>2932</td>
</tr>
<tr>
<td>e</td>
<td>p-NH₂</td>
<td>1228</td>
<td>1668</td>
<td>2282</td>
<td>2940</td>
</tr>
<tr>
<td>f</td>
<td>p-Br</td>
<td>1220</td>
<td>1690</td>
<td>2280</td>
<td>2938</td>
</tr>
<tr>
<td>g</td>
<td>m-NO₂</td>
<td>1218</td>
<td>1910</td>
<td>2280</td>
<td>2932</td>
</tr>
</tbody>
</table>

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 νCH sym. while the band around 2930 cm⁻¹ is assigned to νCH assym.

The vibrations of the C=O group leads to two bands, the first one within the range 1220-1250 cm⁻¹ corresponds to the stretching vibration of the C=O system, i.e. the carbonyl group in the polarized state. The appearance of this band supports the occurrence 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=O stretching vibration, i.e. in its ground state. The position of the C=O band denotes that the group would be involved in the keto-enol tautomerism with the neighbouring CH₂-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 nitrides 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 \(\tilde{v}\) values for the main ir-bands (cf. Fig. 4) show that only the C=0 band correlates fairly with the \(\sigma\)-Hammett constant (\(\rho = 19.5\), \(r = 0.75\)) indicating the direct interaction between the C=0 group and the substituents. For the other bands no good correlation was obtained.

![Graph](image)

Fig (4)

Fig. 4: Wavenumbers-Hammett's constant \(\sigma\) correlation for the main bands of compounds 1\(\alpha\)-\(x\).
REFERENCES