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A CALORIMETRIC STUDY OF THE PROTONATION PROCESS OF SOME INDOLE DERIVATIVES IN ACETONITRILE. CORRELATIONS WITH ELECTRO-OXIDATION AND IONIZATION POTENTIALS

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ABSTRACT

A calorimetric study of the proton transfer process for a series of 1-methyl-2-phenyl 3-substituted indoles in acetonitrile is presented.

A linear regression analysis of the proton transfer and electron transfer data for the gaseous and liquid (acetonitrile) phases leads to the hypothesis that all the substituents affect the protonation and the oxidation processes in the same way, excluding the 3-nitroso derivative.

INTRODUCTION

Proton transfer in the liquid phase and the gas phase, is probably the most studied class of reaction in ion–molecule chemistry [1–9].

All organic compounds, for example, are potential proton acceptors and/or proton donors and may be converted into reactive intermediates by proton transfer processes.

Isodesmic (ion–molecule) processes, such as

$$A_1H + A_2^- = A_1^- + A_2H$$

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or

$$B_1H^+ + B_2 = B_1 + B_2H^+$$

are usually employed, mostly in the gas phase, to emphasize the effect of structural change on the thermodynamic properties of proton transfer reactions for many substituted (A_1 or B_1) and unsubstituted (A_2 or B_2) acids or bases.

Recently developed techniques in gas phase chemistry [10–14] such as ion cyclotron resonance (ICR), high-pressure mass spectrometry (HPMS) and flowing afterglow (FA) have given us a deeper insight into gaseous proton transfer processes. In this way it is possible to study acid–base reactivity in terms of molecule structure and bonding, in the absence of solvent effects.

Furthermore, by using the same proton transfer process in the gas phase and the liquid phase, it is possible to carry out a thermodynamic cycle which allows the solvent effects to be separated from those intrinsic to the molecules and ions [15–17].

Hepler and coworkers [18–21] have stressed the usefulness of expressing the variation in thermodynamic functions ($\delta\,\Delta G$, $\delta\,\Delta H$, $\delta\,\Delta S$) related to the proton transfer processes in terms of "internal" and "external" contributions (i.e. $\delta\,\Delta H = \delta\,\Delta H_{\mathrm{in}} + \delta\,\Delta H_{\mathrm{ex}}$). Internal effects are those intrinsic to the molecules and to the ions (that is the effects related to gaseous isodesmic processes) whereas external effects are derived from solvent interactions with the molecules and ions and are thus related to the solvation process.

The following thermodynamic cycle is used to calculate the external interactions:

$$\begin{tikzcd}
B_1H^+_{(g)} + B_{2(g)} \arrow[r, "\delta\,\Delta P_{i(g)}"] & B_{1(g)} + B_2H^+_{(g)} \arrow[d, "\Delta P_s"] \\
B_1H^+_{(X)} + B_{2(X)} \arrow[r, "\delta\,\Delta P_{i(X)}"] & B_{1(X)} + B_2H^+_{(X)}
\end{tikzcd} \qquad (1)$$

where B_2 (unsubstituted base) is used as reference compound in the proton transfer process for a series of substituted bases B_1. The following relation can be written:

$$\delta\,\Delta P_{i(X)} - \delta\,\Delta P_{i(g)} = [\Delta P_s(B_1) - \Delta P_s(B_1H^+)] - [\Delta P_s(B_2) - \Delta P_s(B_2H^+)]$$

$$\delta\,\Delta P_{i(X)} - \delta\,\Delta P_{i(g)} = \delta\,\Delta P_s \qquad (2)$$

where $\delta\,\Delta P_{i(g)}$ is the gas phase change of any thermodynamic property ($P_i = G, H, S$) from B_1 to B_2. The corresponding value in solvent X is $\delta\,\Delta P_{i(X)}$. The right-hand term of eqn. (2), which represents the solvation of the proton transfer process, is the thermodynamic property for the proton transfer in solvent X, which refers to a gaseous initial thermodynamic state, i.e.

$$\delta\,\Delta P_s = \delta\,\Delta P_i^{g \to X}$$

Moreover, it can be assumed that the $\delta\,\Delta P_{\mathrm{i}}^{\mathrm{g}\to\mathrm{X}}$ term is a measure of external interactions, so that it is reasonable to assume that $\delta\,\Delta P_{\mathrm{i(X)}}$, $\delta\,\Delta P_{\mathrm{i(g)}}$ and $\delta\,\Delta P_{\mathrm{i}}^{\mathrm{g}\to\mathrm{X}}$, which represent the "total", the internal and the external interactions, respectively, can be correlated as in eqn. (3).

$$\delta\,\Delta P_{\mathrm{i(X)}} = \delta\,\Delta P_{\mathrm{i(g)}} + \delta\,\Delta P_{\mathrm{i}}^{\mathrm{g}\to\mathrm{X}} \tag{3}$$

A thermodynamic cycle which allows the comparison of the thermodynamic parameters in the liquid phase, especially half-wave oxidation (or reduction) potentials $E_{1/2}$, and the thermodynamic parameters in the gas phase, such as ionization potentials IP (or electron affinity EA) [22,23], can be also written for electron transfer processes. In fact, for a homogeneous series of 3-substituted indoles the thermodynamic cycle (4) can be constructed

$$\begin{tikzcd}
\mathrm{R{-}H}^{+\cdot}_{\mathrm{(g)}} + \mathrm{R{-}Y}_{\mathrm{(g)}} \arrow[r, "\delta\,\Delta P_{\mathrm{ox(g)}}"] & \mathrm{R{-}H}_{\mathrm{(g)}} + \mathrm{R{-}Y}^{+\cdot}_{\mathrm{(g)}} \arrow[d, "\Delta P_{\mathrm{s}}"] \\
\mathrm{R{-}H}^{+\cdot}_{\mathrm{(g)}} + \mathrm{R{-}Y}_{\mathrm{(X)}} \arrow[r, "\delta\,\Delta P_{\mathrm{ox(X)}}"] & \mathrm{R{-}H}_{\mathrm{(X)}} + \mathrm{R{-}Y}^{+\cdot}_{\mathrm{(X)}}
\end{tikzcd} \tag{4}$$

In this cycle $\delta\,\Delta P_{\mathrm{ox(g)}}$ and $\delta\,\Delta P_{\mathrm{ox(X)}}$ represent, for example, the difference in IP and $E_{1/2}$ values respectively for the unsubstituted R–H (chosen as reference) and the substituted R–Y compounds, and ΔP_{s} represents the solvation energies of molecules and radical cations. From this cycle the following relations can also be written

$$\begin{aligned}\delta\,\Delta P_{\mathrm{ox(X)}} - \delta\,\Delta P_{\mathrm{ox(g)}} = {} & [\Delta P_{\mathrm{s}}(\mathrm{R{-}H}) - \Delta P_{\mathrm{s}}(\mathrm{R{-}H}^{+\cdot})] \\ & -[\Delta P_{\mathrm{s}}(\mathrm{R{-}Y}) - \Delta P_{\mathrm{s}}(\mathrm{R{-}Y}^{+\cdot})]\end{aligned}$$

and then

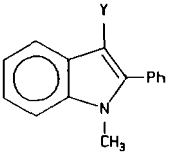
$$\delta\,\Delta P_{\mathrm{ox(X)}} - \delta\,\Delta P_{\mathrm{ox(g)}} = \delta\,\Delta P_{\mathrm{s}} \tag{5}$$

The $\delta\,\Delta P_{\mathrm{s}}$ term is assumed to be the difference, in an appropriate solvent, between the $E_{1/2}$ values of the two redox couples, which refer to a gaseous initial thermodynamic state, so that

$$\delta\,\Delta P_{\mathrm{s}} = \delta\,\Delta P_{\mathrm{ox}}^{\mathrm{g}\to\mathrm{X}}$$

According to Hepler and coworkers, $\delta\,\Delta P_{\mathrm{ox(X)}}$ represents the overall oxidation process, $\delta\,\Delta P_{\mathrm{ox(g)}}$ the effects intrinsic to molecules and radical cations and $\delta\,\Delta P_{\mathrm{ox}}^{\mathrm{g}\to\mathrm{X}}$ the effects derived from solvent interactions with molecules and radicals.

The aim of this work was to study the effects of the substituent on the protonation of 1-methyl-2-phenyl 3-substituted indole derivatives **1**–**15** and to compare them with the substituent effects found previously for the oxidation processes of the same series of compounds in the gas phase and the liquid phase [22].



1 Y = Me
2 Y = Cl
3 Y = CHO
4 Y = CH$_2$OH
5 Y = NO
6 Y = NO$_2$
7 Y = COMe
8 Y = SMe
9 Y = SPh
10 Y = N$_2$Ph
11 Y = MeCH=CH$_2$
12 Y = MeCH=CHMe
13 Y = CH(OH)Ph
14 Y = CH$_2$Ph
15 Y = H

It may be expected that if the substituent at the C_3 position affects both the protonation [24–29] and the oxidation processes of the derivatives **1–15** in the same way then the thermodynamic properties of the protonation and the oxidation (in the liquid and the gas phases) can be related by a linear relationship.

For this purpose it is convenient to use a monoparametric linear regression analysis. Total standard deviation, standard deviation of the slope and of the intercept, correlation coefficient values and the Student *t* test for the above-cited values supply the precise form of the mathematical function relating the two variables and test how the experimental results support the theoretical relationship within the limits of the experimental error of the measurements [30–35]. However, the significance level of these relations only allows the experimental results to be compared and explained in terms of probabilities.

EXPERIMENTAL AND PROCEDURE

All studied compounds were prepared as indicated in ref. 36. The Tronac (model 458) calorimeter was used. The vessel calorimeter was a rapid-response, glass vacuum Dewar of maximum capacity 25 cm^3. The burette volume was 2 cm^3 and the measured titrant delivery rate 0.49373 cm^3 min^{-1}. The thermostat was maintained at 298.15 ± 0.0002 K by employing a Tronac P.T.C.-41 precision temperature controller. Potential vs. time measurements were made using a Fluke 88100 model digital voltmeter. The unbalance (volts) of the bridge of the calorimeter was fed into a Hitachi 561-10002/P strip chart recorder and into a digital voltmeter, which in turn was connected to an Olivetti M24 computer. Data were acquired by the computer via a data acquisition system and subsequently read and converted into enthalpy values using a BASIC program [37] run on the Olivetti M24. Data obtained using the chart recorder may be slightly different from those obtained using the computer and they also give the shape of the reaction.

Acetonitrile (C. Erba RS for UV–IR) and hydrochloric acid (Merck 12.48 M) were used. Acid concentration was checked by potentiometric titration. 25 ml of indole derivatives solutions, ranging from 5.64 10^{-4} M to 1.51 ×

10^{-3} M, were placed in a vessel. Acid solution, containing excess HCl equivalents from 5% to 30%, was subsequently added, via a precision burette.

The protonation process of the indole derivatives R–Y in acetonitrile solutions can be represented as

$$\text{R–Y}_{C_2(\text{X})} + \text{H}^+_{C_2(\text{X})} = \text{R–YH}^+_{C_2(\text{X})} \tag{6}$$

The partial molar enthalpy of protonation related to process (6), $\Delta\overline{H}_6$, was obtained by the following experimental measurements.

(a) The partial molar enthalpy of reaction ΔH_7 of R–Y indole derivative dissolved in acetonitrile at concentration C_2 with 12.48 M HCl (also dissolved in acetonitrile) at concentration C_1

$$\text{R–Y}_{C_2(\text{X})} + \text{H}^+_{C_1(\text{X})} + \text{ClO}^-_{4\,C_1(\text{X})} = \text{R–YH}^+_{C_2(\text{X})} + \text{ClO}^-_{4\,C_2(\text{X})} \tag{7}$$

(b) The partial molar enthalpy of dilution, $\Delta\overline{H}_8$, of the same amount of HCl, at concentration $C_{1(\text{X})}$, dissolved in 25 ml of acetonitrile

$$\text{H}^+_{C_1(\text{X})} + \text{ClO}^-_{4\,C_1(\text{X})} = \text{H}^+_{C_2(\text{X})} + \text{ClO}^-_{4\,C_2(\text{X})} \tag{8}$$

So that the molar enthalpy of process (6) can be obtained by subtracting $\Delta\overline{H}_8$ from $\Delta\overline{H}_7$.

For each solution the $\Delta\overline{H}_6$ value refers to the reaction of 1 mol of R–Y and 1 mol of protons both dissolved at infinite dilution in 1000 g of solvent, yielding 1 mol of R–YH$^+$ diluted in the same amount of solvent.

In processes (7) and (8) concentrations ranging from 5.6×10^{-4} M to 1.5×10^{-3} M were used. Therefore, the $\Delta\overline{H}$ related to these processes were assumed to be equal to ΔH° [38]. Regarding the subtraction of $\Delta\overline{H}_8$ from $\Delta\overline{H}_7$ the following considerations must be taken into account.

Let us consider the equation

$$Q_\text{t} = Q_\text{p} + Q_\text{d}$$

where Q_t is the overall heat term, Q_p the heat term due to the protonation and Q_d the dilution heat term. The equation can be written in the form

$$Q_\text{t} = n_1\,\Delta\overline{H}_6 + n_2\,\Delta\overline{H}_8 \tag{9}$$

where n_1 and n_2 are the moles respectively of indole derivatives and of hydrochloric acid, and $\Delta\overline{H}_6$ and $\Delta\overline{H}_8$ (as previously shown) are the partial molar enthalpies of protonation and dilution respectively.

Bearing in mind that $n_2 = n_1\,(1 + \beta)$, where β is the excess percentage of n_2 with respect to n_1, one can write

$$Q_\text{t} = n_1\,\Delta\overline{H}_6 + (1 + \beta)n_1\,\Delta\overline{H}_8 \tag{10}$$

and finally the enthalpy values of protonation $\Delta\overline{H}_6$ can be obtained as

$$\Delta\overline{H}_6 = (Q_\text{t}/n_1) - \Delta\overline{H}_8(1 + \beta) \tag{11}$$

where Q_t/n_1 represents the partial molar enthalpy of the overall heat term with respect to the indole derivatives ($\Delta\overline{H}_7$).

A constant value for $\Delta\overline{H}_6$ is obtained on varying β.

RESULTS AND DISCUSSION

Table 1 lists the enthalpy values for the protonation of 1-methyl-2-phenyl 3-substituted indoles **1–15** and also the *para* substituent constants σ_p.

For the sake of comparison it is convenient to express the protonation enthalpy values, $\Delta H°$, of the indole derivatives, as the difference between their values and that of the reference compound **15** (Y = H) so that

$$\delta\,\Delta H° = \Delta H_Y^\circ - \Delta H_H^\circ$$

refers to the proton transfer process

$$R\text{–}Y_{(X)} + R\text{–}H_{2(X)}^{+} = R\text{–}YH_{(X)}^{+} + R\text{–}H_{(X)}$$

These values (Table 2) show how the protonations for the derivatives bearing electron-withdrawing substituents are endothermic with respect to reference compound **15**, while for the derivatives with electron-donating substituent groups the reverse is true.

TABLE 1

Enthalpy values for the protonation process of 1-methyl-2-phenyl 3-substituted indoles **1–15** in acetonitrile at 25 ° C plus *para* substituent values

Compound	Y	ΔH (kJ mol^{-1})	σ_p
1	Me	−5.57	−0.17 [a]
2	Cl	−3.34	0.23 [a]
3	CHO	6.01	0.22 [a]
4	CH_2OH	−3.35	0.054 [b]
5	NO	−54.0	0.12 [a]
6	NO_2	11.4	0.78 [a]
7	COMe	3.36	0.52 [a]
8	SMe	−6.70	−0.05 [a]
9	SPh	−4.00	0.025 [b]
10	N_2Ph	−3.81	0.034 [b]
11	$MeCH{=}CH_2$	−5.62	−0.046 [b]
12	MeCH=CHMe	−8.73	−0.18 [b]
13	CH(OH)Ph	−1.99	0.11 [b]
14	CH_2Ph	−4.10	0.021 [b]
15	H	−2.47	0.00

[a] Values from ref. 39.

[b] Values calculated in this work (see text).

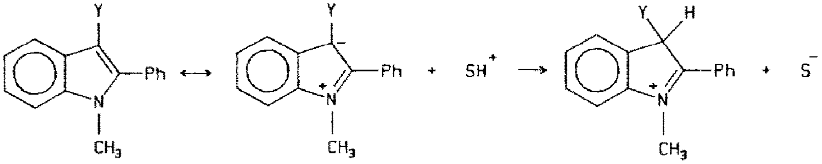
TABLE 2

Differences with respect to unsubstituted compound **15** of the enthalpy of protonation and of the oxidation and ionization potentials for 1-methyl-2-phenyl 3-substituted indoles

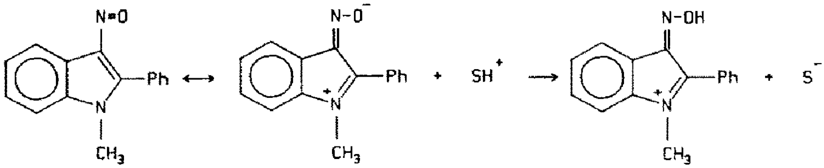
Compound	Y	$\delta \Delta H$ [a] (kJ mol^{-1})	$\delta E_{1/2}$ [b] (V)	δIP [b] (eV)
1	Me	−3.10	−0.095	−0.15
2	Cl	−0.87	0.12	0.06
3	CHO	8.48	0.44	0.50
4	CH_2OH	−0.88	0.01	0.13
5	NO	−51.5	0.08	0.06
6	NO_2	13.8	0.65	0.73
7	COMe	5.83	0.32	0.30
8	SMe	−4.23	−0.13	0.00
9	SPh	−1.53	0.025	0.01
10	N_2Ph	−1.34	0.05	0.03
11	$MeCH{=}CH_2$	−3.15	−0.22	−0.33
12	MeCH=CHMe	-6.26	−0.13	−0.13
13	CH(OH)Ph	0.48	0.035	0.01
14	CH_2Ph	−1.63	−0.065	−0.16
15	H	0.0	0.00	0.00

[a] Values from data of Table 1.
[b] Values from ref. 22.

The experimental data are compatible with the usual description of the behaviour of the indole series in terms of the resonance effect. There is a significant delocalization of electron density from the nitrogen atom to C_3, which confirms that this is the most reactive site for the protonation processes [40]. For this reason Scheme 1 can be hypothesized.



The very large negative enthalpy of protonation, obtained for compound **5** (Y = NO) can be explained in terms of a different protonation mechanism, as shown in Scheme 2; this is also confirmed by the chemical reactivity of this nitroso compound in the presence of acid and benzoyl chloride [41].



Finally, for compound **2** (Y = Cl) the poor negative value (chlorine being an electron-withdrawing substituent) can be explained by the fact that the donor effect of the chlorine atom prevails over its electron-withdrawing power.

To verify whether the substituents at the C_3 position affect the protonation and the oxidation processes in the same way as shown previously, a comparison of the proton transfer processes in the liquid phase and the electron transfer processes in gaseous and liquid phases was considered to be a useful tool.

Table 2 lists the $\delta E_{1/2}$ (V) and δIP (eV) values for the indole derivatives studied. From these values and those of Table 1, the following correlations were examined critically, by means of a linear monoparametric regression analysis: (i) $\delta\,\Delta H$ vs. δIP; (ii) $\delta\,\Delta H$ vs. $\delta E_{1/2}$; (iii) $\delta\,\Delta H$ vs. σ_p.

For all these correlations the null hypotheses considered were: (1) for the intercept $a = 0$; (2) for the slope $b = 0$.

For the relation (iii) the regression was not forced through the origin. An intercept was obtained with the least-squares treatment, but it was normally indistinguishable from zero.

The null hypotheses were tested by using the Student t test. The t values of a and b were calculated from the expressions

$$t_a = (a - A)/s_a$$

$$t_b = (b - B)/s_b$$

(where A and B are variables which can be put equal to zero and s_a and s_b are the standard deviations of a and b), and these were compared with those of a set of t tables. If $t > t_{\mathrm{CL},n-2}$ (where $n - 2$ is the degree of freedom and CL the confidence level for the significance of the regression) then for $\mathrm{CL} < 0.95$ the null hypothesis is accepted (chemical hypothesis) while for $\mathrm{CL} > 0.999$ its rejection is highly significant.

$\delta\,\Delta H$ vs. δIP

It was found that there is a good relation from the statistical viewpoint (Table 3) between the two variables if the compound **5** (Y = NO) is removed from the set. This signifies that the substituent group at C_3 affects the protonation and the ionization (in the gas phase) processes in the same way.

$\delta\,\Delta H$ vs. $\delta E_{1/2}$

For this relation too the correlation is highly significant if compound **5** (Y = NO) is excluded (Table 4). This implies that the protonation and the oxidation (in the liquid phase) are affected in the same way by the substituents at the C_3 position.

$\delta\,\Delta H$ vs. σ_p

TABLE 3

Results of monoparametric regression analysis of $\delta\,\Delta H$ vs. δIP for indole series

n	14
Intercept	-0.89
Slope	18.10
SD of intercept	0.58
SD of slope	2.11
SD of reg.	2.11
r	0.93
n.h.: intercept = 0	CL < 0.95
n.h.: slope = 0	CL > 0.999

n.h., null hypothesis.

TABLE 4

Results of monoparametric regression analysis of $\delta\,\Delta H$ vs. $\delta E_{1/2}$ for indole series

n	14
Intercept	-1.15
Slope	21.74
SD of intercept	0.40
SD of slope	1.66
SD of reg.	1.44
r	0.97
n.h.: intercept = 0	0.95 < CL < 0.99
n.h.: slope = 0	CL > 0.999

This linear regression gives prominence to substitution effects. For seven indole derivatives, for which the substituent constant values σ_p of corresponding benzoic acid deivatives are reported in Table 1, a significant correlation was found (Table 5). From the linear regression equation, obtained by reversing the variables (i.e. σ_p vs. $\delta\,\Delta H$) the substituent

TABLE 5

Results of monoparametric regression analysis of $\delta\,\Delta H$ vs. σ_p for indole series

n	7
Intercept	-0.98
Slope	17.52
SD of intercept	1.61
SD of slope	4.23
SD of reg.	3.48
r	0.88
n.h.: intercept = 0	CL < 0.99
n.h.: slope = 0	0.99 < CL < 0.999

constants for the remaining indoles were calculated. These values seem to be in agreement with those of the literature.

In summary, it can be concluded that for the studied 1-methyl-2-phenyl 3-substituted indoles **1–15** the electron-withdrawing substituents disfavour protonation and oxidation (in the liquid and the gas phases), while for the electron-donating groups the reverse is true.

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