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THERMODYNAMICS OF ELECTRON TRANSFER PROCESSES IN LIQUID AND GAS PHASES. PART II. CORRELATIONS OF ELECTRO-OXIDATION AND IONIZATION POTENTIALS WITH SUBSTITUENT CONSTANTS FOR SOME *N,N*-DIMETHYLANILINE DERIVATIVES

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ABSTRACT

The electron transfer processes in the oxidation reactions of a series of *N,N*-dimethyl-4-substituted anilines in liquid and gaseous phases were studied. By means of a linear regression analysis, half-wave oxidation potentials in acetonitrile, ionization potentials in the gaseous phase, substituent constants and ionization constants of conjugated acids in water or water–alcohol mixtures are related. A thermodynamic cycle allows the calculation of the solvation energies of both radical cations and parent free bases.

INTRODUCTION

A previous paper [1] showed that the solvation factors affecting electron transfer processes can be evaluated from a comparison between thermodynamic parameters in the liquid phase (x), especially oxidation (or reduction) potentials $E_{1/2}$ and thermodynamic parameters in the gas phase (g) such as ionization potentials (IP) or electron affinities (EA).

Indeed, for a one-electron reversible oxidation process in a series of substituted compounds R–Y containing the same oxidizable group R and differing only in the nature of the substituent Y, the following thermodynamic cycle can be written:

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

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where $\delta\Delta P_{ox}(g)$ and $\delta\Delta P_{ox}(x)$ represent the differences in ΔIP and $\Delta E_{1/2}$ values respectively for the unsubstituted R–H compound chosen as a 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 drawn:

$$\delta\Delta P_{ox}(x) - \delta\Delta P_{ox}(g) = [\Delta P_s(\text{R–H}) - \Delta P_s(\text{R–H}^{\cdot +})] - [\Delta P_s(\text{R–Y}) - \Delta P_s(\text{R–Y}^{\cdot +})]$$

and then

$$\delta\Delta P_{ox}(x) - \delta\Delta P_{ox}(g) = \delta\Delta P_s$$

The $\delta\Delta P_s$ term can be assumed as the difference, in an appropriate solvent, between the $\Delta E_{1/2}$ values of the two redox couples, which refer to a gaseous initial thermodynamic state, so that $\delta\Delta P_s = \delta\Delta P_{ox}^{g\to x}$.

According to Hepler [2,3] and Hepler and O'Hara [4], $\delta\Delta P_{ox}(x)$ represents the overall oxidation process, $\delta\Delta P_{ox}(g)$ the "internal" effects and $\delta\Delta P_{ox}^{g\to x}$ the "external" ones. "Internal" effects are those intrinsic to molecules and radicals, whereas "external" effects derive from solvent interactions with molecules and radicals.

To separate the solvent effects from the intrinsic effects, the difference between the thermodynamic properties in solution and in the gas phase need to be known. Indeed, such a difference, which depends on the different effects of molecular structure on the solvation properties of the uncharged molecules and radical cations, causes a non-linear relationship of gas phase vs. solution thermodynamic properties. Thus, for a series of compounds a critical examination of correlations between $\delta\Delta IP_v$ and $\delta\Delta E_{1/2}$, $\delta\Delta G_{ox}^{g\to x}$ and $\delta\Delta G_{ox}(g)$, $\delta\Delta E_{1/2}$ and σ-substituent constant values etc., allows an evaluation of the effects of molecular structure, of substituent groups, of the medium etc., on the overall oxidation process for homologous or different series of compounds to be made.

Furthermore, these correlations are very useful in predicting some thermodynamic properties (in both liquid and gas phases) for other derivatives of the studied series using a known property as input data.

In every case the correlations have to be studied from the statistical viewpoint by using a linear regression analysis which supplies the precise form of the mathematical function relating the two variables and tests how the experimental results support the theoretical relationship within the limits of the experimental errors of measurement.

In this context, more useful tests are the standard deviations of the slope and of the intercept, the total standard deviation and the Student-*t* test for the intercept, slope and the coefficient correlation values of the regression [5–10].

It is also worth noting that the degree of significance (highly significant, significant etc.) for these correlations allows the experimental results to be compared and explained only in terms of probability. The introduction of subjective data (confidence level, error distribution) is the reason why the statistical analysis cannot supply absolute answers.

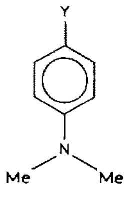
In a previous paper [1], through a linear regression analysis, we reported an accurate correlation between the vapour phase vertical ionization potentials and the liquid phase oxidation potentials in acetonitrile for heterocyclic systems such as 1-methyl-2-phenyl-3-substituted indoles and 1,3-disubstituted-2-phenyl indolizines respectively.

In the present paper, we report the results obtained on examining the correlations between oxidation potentials in acetonitrile (determined electrochemically or taken from the literature [11]), vertical ionization potentials (evaluated from electronic spectra [12]), substituent constants (σ_p and σ_p^+) [13] and some ionization constants of the corresponding conjugated acids (pK_A) [14] for N,N-dimethyl 4-substituted anilines **1**–**12**.

It is well-known that electron-donor or electron-withdrawing substituents exert a considerable resonance stabilization effect on the radical cations derived from the compounds **1**–**12** [15]. On the other hand, σ_m and σ_p values represent the "substituent constant" effect in the Hammett equation and are inclusive of resonance and inductive effects. However, where a para substituent can contribute significantly to through-resonance in the molecule, σ_p values vary for different reactions.

For this reason σ_p^+ values are also considered. Therefore, the examination of the correlations $\delta\Delta E_{1/2}$ vs. σ_p and $\delta\Delta E_{1/2}$ vs. σ_p^+, allows better correlation to be chosen, and also allows us to ascertain if there is direct interaction by the conjugation effect.

Furthermore, a comparison of the correlations for the N,N-dimethylanilines **1**–**12** and the previously studied indoles and indolizines [1] can give useful information about the mechanism of the electron transfer process in both the liquid and gaseous phase for the three series of compounds.



1–12

1 Y = OMe
2 Y = Me
3 Y = H
4 Y = Cl
5 Y = CHO
6 Y = NO_2
7 Y = NO
8 Y = N_2Ph
9 Y = COMe
10 Y = CH_2PhNMe_2
11 Y = CH(OH)Ph
12 Y = CH(OH)Et

TABLE 1

Differences with respect to the unsubstituted compound **3** of the oxidation and ionization potentials, solvation free energy, ionization free energy for *N*,*N*-dimethyl-4-substituted anilines plus σ_p, σ_p^+ and pK_A values

Compound	Y	$\delta\Delta E_{1/2}$ (V)	$\delta\Delta IP_v$ (eV)	$\delta\Delta G_{ox}(g)$ (kJ mol^{-1})	$\delta\Delta G_{ox}^{g\to x}$ (kJ mol^{-1})	σ_p	σ_p^+	pK_A (H_2O)	pK_A (H_2O/ C_2H_5OH)
1	OMe	−0.22 [a]	−0.23 [c]	−22.19	43.42	−0.27 [d]	−0.78 [d]	5.89 [f]	5.09 [f]
2	Me	−0.06 [a]	−0.20 [c]	−19.30	25.09	−0.17 [d]	−0.31 [d]	5.50 [f]	4.88 [f]
3	H	0.00 [a,b]	0.00 [c]	0.00	0.00	0.00 [d]	0.00 [d]	5.12 [f]	4.39 [f]
4	Cl	0.13 [a]	0.15 [c]	14.47	−27.01	0.23 [d]	0.11 [d]	4.34 [f]	3.29 [f]
5	CHO	0.27 [b]	0.25 [c]	24.12	−50.17	0.22 [d]	0.58 [e]	3.84 [g]	3.31 [g]
6	NO_2	0.48 [a]	0.49 [c]	47.28	−93.59	0.78 [d]	0.79 [d]	0.61 [f]	1.13 [g]
7	NO	0.12 [b]	–	–	–	0.12 [d]	0.26 [e]	4.37 [g]	3.48 [f]
8	N_2Ph	0.10 [b]	–	–	–	0.64 [d]	0.21 [e]	1.61 [g]	1.68 [g]
9	COMe	0.24 [b]	–	–	–	0.52 [d]	0.51 [e]	2.24 [g]	2.14 [g]
10	CH_2PhNMe_2	−0.11 [b]	–	–	–	−0.16 [e]	−0.24 [e]	–	–
11	CH(OH)Ph	−0.02 [b]	–	–	–	−0.04 [e]	−0.05 [e]	–	–
12	CH(OH)Et	−0.05 [b]	–	–	–	−0.08 [e]	−0.11 [e]	–	–

[a] Values calculated from ref. 11.

[b] Values determinated by us (see experimental section).

[c] Values calculated from ref. 12.

[d] Values calculated from ref. 13.

[e] Values calculated by us (see text).

[f] Values from ref. 14.

[g] Values calculated by us (see text).

EXPERIMENTAL PROCEDURE

Compounds **3** (Fluka), **5** (Fluka) and **8** (Erba) were used as purchased. Compounds **6** [16], **9** [17], **10** [18], **11** [19] and **12** [19] were prepared as described in the literature. 4-Nitroso-*N*,*N*-dimethylaniline **7** was synthesized by the following procedure. The 4-nitroso-*N*,*N*-dimethylaniline hydrochloride (70 g), prepared as described in the literature [20], was poured into 10% aqueous NaOH (100 ml) and then another 400 ml of the same solution were added with stirring. After 1 h, the green solid was filtered under vacuum and washed with water (5 × 50 ml) on a Buchner funnel. The separated nitroso compound was dried in air after crystallization from ligroin (80–100 ° C) and had a melting point of 86 ° C.

The electrochemical data for the aniline derivatives **1**–**12** reported in Table 1 all refer to acetonitrile solvent and to a platinum anode. The electrochemical behaviour of several derivatives (**3** and **5**–**12**) was tested in our laboratory by a three-electrode multifunction assembly (Amel 471) using a platinum disc (Amel 492) of about 1 mm in diameter as the working electrode, an Ag/0.1 M $AgClO_4$ with a fitted glass disc of fine porosity as reference electrode and a platinum wire as auxiliary electrode. Acetonitrile (MeCN) (Erba, spectrophotometric grade), used as solvent, was purified by distillation over CaH_2, P_2O_5 and then over CaH_2 again. $(C_2H_5)_4$ $NClO_4$ (Erba, RS grade for polarography), used as supporting electrolyte, was vacuum dried at 60 ° C for 3 days. Argon (99.99%) was used to deoxygenate the test solution. The temperature (20 ° C), was kept constant within 0.1° C. All the anilines examined exhibit a "quasi-reversible" charge transfer as tested by cyclic voltammetric experiments in the sweep rate range 0.05–1.0 V s^{-1}.

A program which supplies a linear regression analysis with total standard deviation, slope and intercept deviations, correlation coefficients and null hypotheses, $a = 0$, $b = 0$, $b = 1$ and $b_1 = b_2$ (where a is the intercept and b the slope of the regression equation), and the Student t-test for all the above values was run on an Olivetti M20ST computer.

RESULTS AND DISCUSSION

Table 1 lists the $\delta\Delta E_{1/2}$ (V), $\delta\Delta \mathrm{IP_v}$ (eV), $\delta\Delta G_{ox}(g)$ (kJ mol^{-1}), $\delta\Delta G_{ox}^{g\rightarrow x}$ (kJ mol^{-1}), σ_p, σ_p^+ and pK_A values for the *N*,*N*-dimethyl-4-substituted-anilines **1**–**12**. From these values the following correlations were critically examined by means of a linear regression analysis:

(I) $\delta\Delta \mathrm{IP_v}$ vs. $\delta\Delta E_{1/2}$

(II) $\delta\Delta G_{ox}^{g\rightarrow x}$ vs. $\delta\Delta G_{ox}(g)$

(III) $\delta\Delta E_{1/2}$ vs. σ_p and σ_p^+

(IV) $\delta\Delta IP_v$ vs. σ_p and σ_p^+

(V) pK_A vs. σ_p and σ_p^+

For all the correlations the null hypotheses considered were: (1) for the intercept $a = 0$; (2) for the slope $b = 0$ and $b = 1$; (3) for the correlation coefficient $r = 0$. Furthermore, for the correlations (III) and (IV), the null hypothesis $b_1 = b_2$ was also considered (b_1 and b_2 being the slopes for the same series in the gaseous and liquid phases or the slopes of two different series in the gaseous or in the liquid phase).

This allows a very important statistical comparison in organic physical chemistry when, for instance, small variations in Hammett's constant ρ are studied as a function of the medium variation. Incidentally, a comparison between the reaction constants is possible by means of the expression $t_b = (b_1 - b_2 - A)/S(b_1 - b_2)$, if it could be verified that the standard errors of the two series are not statistically different.

For the Hammett equation the regression was not forced through the origin. An intercept was drawn with the least-squares treatment, but it was normally indistinguishable from zero.

The null hypotheses were tested by using the Student t-test. Indeed the t values of a, b and r were compared with those of a set of t'-Tables. The t values of a, b and r were calculated by means of the expressions: $t_a = (a - A)/S_a$; $t_b = (b - B)/S_b$; $t_b = (b_1 - b_2 - A)/S(b_1 - b_2)$; $t_r = |r|[(n-2)/(1 - r^2)]^{1/2}$, where $A = 0$, $B = 0$ or 1 and S_a and S_b are the standard deviations of a and b. If $t > t'_{CL,n-2}$ (where $n = 2$ is the degree of freedom and CL the confidence level for significance of the regression), then for CL < 0.95 the null hypothesis is accepted (in agreement with the chemical hypothesis), while for CL > 0.999 its rejection is highly significant [5–10].

$\delta\Delta IP_v$ *vs.* $\delta\Delta E_{1/2}$

The linear regression is highly significant (Table 2). The coefficient of regression (1.08) shows that there is a small attenuation of the substituent effect from the gas to the liquid phases.

A comparison between the slope values for the *N*,*N*-dimethyl-4-substituted aniline series and the corresponding values for the indole and indolizine series [1] allows the following scale to be obtained: indoles (1.11) > anilines (1.08) > indolizines (0.81). In every case the substituent effect is greater in the gaseous phase: the difference in the attenuation effect could be attributed to the greater influence of the substituents on the resonance stabilization in the liquid phase.

Moreover, the highly significant correlation $\delta\Delta IP_v$ vs. $\delta\Delta E_{1/2}$ could mean that the energy differences between the vertical ionization potentials (IP_v)

TABLE 2

Linear regression of $\delta\Delta IP_v$ vs. $\delta\Delta E_{1/2}$ and $\delta\Delta G_{ox}^{g\to x}$ vs. $\delta\Delta G_{ox}(g)$ for *N,N*-dimethyl-4-substituted aniline series

	$\delta\Delta IP_v$ vs. $\delta\Delta E_{1/2}$	$\delta\Delta G_{ox}^{g\to x}$ vs. $\delta\Delta G_{ox}(g)$
n [a]	6	6
Intercept	−0.32	−3.09
Slope	1.08	−1.88
SD [b] of intercept	0.03	2.28
SD of slope	0.10	0.09
SD of regression	0.06	5.35
r [c]	0.98	0.99
NH [d]: intercept = 0	CL [e] < 0.95	CL < 0.95
NH: slope = 0	CL > 0.999	CL > 0.999
NH: slope = 1	CL < 0.95	CL > 0.999
NH: $r = 0$	CL > 0.999	CL > 0.999

[a] *n*, number of points.
[b] SD, standard deviation.
[c] *r*, correlation coefficient.
[d] NH, null hypothesis.
[e] CL, confidence level.

and adiabatic ionization potentials (IP_a) are not considerable. This suggests that the geometry of the nitrogen atom is the same for the anilines and the corresponding radical cations [21]. Usually, a highly significant correlation is found between ΔIP_a vs. $\Delta E_{1/2}$, since both are derived from adiabatic measurements.

$\delta\Delta G_{ox}^{g\to x}$ *vs.* $\delta\Delta G_{ox}(g)$

It is usually hypothesized that a linear correlation between $\Delta E_{1/2}$ and ΔIP_v (or ΔIP_a) is to be expected if the free energy of solvation is constant within a series of compounds or if there is an approximately linear function between the free energy of solvation and ionization potential. We have previously found that the differential solvation factors do not cause deviations from linear energy correlations of gas vs. thermodynamic properties, for both the indolizine and indole series [1].

The highly significant regression for the *N,N*-dimethyl-4-substituted-aniline series (Table 2) also confirms that the radical cation exists in an approximately tetrahedral geometry at the nitrogen atom as in the parent free base.

$\delta\Delta E_{1/2}$ *vs.* σ_p *and* σ_p^+

This linear regression gives prominence to substituent effects. The sign and the values of the slope, which can be identified with the reaction

TABLE 3

Linear regression of $\delta\Delta E_{1/2}$ vs. σ_p^+ and $\delta\Delta E_{1/2}$ vs. σ_p for *N*,*N*-dimethyl-4-substituted aniline series [a]

	$\delta\Delta E_{1/2}$ vs. σ_p^+	$\delta\Delta E_{1/2}$ vs. σ_p
n	5	9
Intercept	0.08	0.01
Slope	0.45	0.48
SD of intercept	0.03	0.05
SD of slope	0.05	0.11
SD of regression	0.06	0.12
r	0.98	0.85
NH: intercept = 0	CL < 0.95	CL < 0.95
NH: slope = 0	0.99 < CL < 0.999	0.99 < CL < 0.999
NH: slope = 1	0.99 < CL < 0.999	0.99 < CL < 0.999
NH: $r = 0$	0.99 < CL < 0.999	0.99 < CL < 0.999

[a] For meaning of symbols, see footnote to Table 2.

constant ρ, are able to give reliable information about the reaction mechanism. For the aniline derivatives, the regression is significant (Table 3) using both σ_p and σ_p^+ values. By reversing the variables (i.e. σ_p and σ_p^+ vs. $\delta\Delta E_{1/2}$), σ_p and σ_p^+ values for some aniline derivatives have been calculated (Table 1).

As the standard errors of the corresponding linear regression ($\delta\Delta E_{1/2}$ vs. σ) are not statistically different, it is possible to compare the reaction constants (ρ) for the indole, indolizine and aniline series: indoles (0.98) > anilines (0.48) > indolizines (0.33). This sequence provides a picture of the substituent effects on the electron transfer processes of the three series of compounds.

$\delta\Delta IP_v$ vs. σ_p and σ_p^+

It is noteworthy that while $\delta\Delta \mathrm{IP_v}$ vs. σ_p^+ is significant, $\delta\Delta \mathrm{IP_v}$ vs. σ_p is highly significant (Table 4). This is not surprising because it is well known that in the gaseous phase the resonance effect is attenuated with respect to that in the liquid phase.

Again, after standard error comparison from the $\delta\Delta \mathrm{IP_v}$ vs. σ relation, the sequence for the reaction constants (ρ), indoles (1.12) > anilines (0.72) > indolizines (0.25), was found to be very similar to that observed for the liquid phase.

A statistical comparison of the reaction constants, for the anilines (**1**–**12**) studied in the liquid and gaseous phases, obtained by properly varing the σ_p and σ_p^+ values, justifies the use of both the substituent constant values. In fact, in every case the values of the null hypotheses ($\rho(\mathrm{MeCN}) = \rho(\mathrm{g})$) show

TABLE 4

Linear regression of $\delta\Delta IP_v$ vs. σ_p^+ and $\delta\Delta IP_v$ vs. σ_p for *N*,*N*-dimethyl-4-substituted aniline series [a]

	$\delta\Delta IP_v$ vs. σ_p^+	$\delta\Delta IP_v$ vs. σ_p
n	5	6
Intercept	0.06	−0.02
Slope	0.49	0.72
SD of intercept	0.04	0.03
SD of slope	0.08	0.08
SD of regression	0.09	0.07
r	0.96	0.97
NH: intercept = 0	$CL < 0.95$	$CL < 0.95$
NH: slope = 0	$0.99 < CL < 0.999$	$CL > 0.999$
NH: slope = 1	$0.99 < CL < 0.999$	$0.95 < CL < 0.99$
NH: $r = 0$	$0.99 < CL < 0.999$	$CL > 0.999$

[a] For meaning of symbols, see footnote to Table 2.

that the reaction constants in the liquid and in the gas phases are not significantly different ($CL < 0.95$).

$\delta p K_A$ *vs.* σ_p *and* σ_p^+

A statistical comparison of δpK_A vs. σ_p and σ_p^+ with pK_A values obtained in water and in water–alcohol (50% v/v) mixtures shows that both pK_a values are reliable. Indeed, the above correlations in water and in water–alcohol mixtures are highly significant both for σ_p and σ_p^+ (Tables 5 and 6). Moreover, using the pK_A vs. σ_p and σ_p^+ linear regression, some pK_A

TABLE 5

Linear regression of δpK_A vs. σ_p and δpK_A vs. σ_p^+ for *N*,*N*-dimethyl-1,4-substituted aniline series in water [a]

	δpK_A vs. σ_p	δpK_A vs. σ_p^+
n	4	4
Intercept	0.11	0.53
Slope	5.31	4.71
SD of intercept	0.30	0.32
SD of slope	0.73	0.75
SD of regression	0.53	0.60
r	0.98	0.98
NH: intercept = 0	$CL > 0.999$	$CL > 0.999$
NH: slope = 0	$CL > 0.999$	$CL > 0.999$
NH: slope = 1	$CL > 0.999$	$CL > 0.999$
NH: $r = 0$	$CL > 0.999$	$CL > 0.999$

[a] For meaning of symbols, see footnote to Table 2.

TABLE 6

Linear regression of δpK_A vs. σ_p and δpK_A vs. σ_p^+ for *N*,*N*-dimethyl-4-subsituted aniline series in water–alcohol mixtures [a]

	δpK_A vs. σ_p	δpK_A vs. σ_p^+
n	5	4
Intercept	0.26	0.38
Slope	2.60	1.67
SD of intercept	0.17	0.34
SD of slope	0.01	0.80
SD of regression	0.34	0.55
r	0.99	0.83
NH: intercept = 0	CL < 0.95	CL > 0.999
NH: slope = 0	CL > 0.999	CL > 0.999
NH: slope = 1	CL > 0.999	CL > 0.999
NH: $r = 0$	CL > 0.999	CL > 0.999

[a] For meaning of symbols, see footnote to Table 2.

values in water and in water–alcohol mixtures were also calculated (Table 1).

Finally, the $\delta\Delta E_{1/2}$ or $\delta\Delta IP_v$ values for *N*,*N*-dimethyl-4-substituted anilines **1**–**12** and 1-methyl-2-phenyl-3-substituted indoles were also compared.

The correlation $\delta\Delta E_{1/2}$ (anilines) vs. $\delta\Delta E_{1/2}$ (indoles) (Table 7) for compounds bearing the same substituent groups in the 4 and 3 position respectively, is highly significant and shows a slope value (0.66) lower than unity. This fact allows us to suggest that, in the liquid phase, the same mechanism of reaction occurs for the two series.

TABLE 7

Linear regression of $\delta\Delta E_{1/2}$ vs. $\delta\Delta E_{1/2}$, $\delta\Delta IP_v$ vs. $\delta\Delta IP_v$ between *N*,*N*-dimethyl-4-substituted aniline and the indole series [a]

	$\delta\Delta E_{1/2}$ vs. $\delta\Delta E_{1/2}$	$\delta\Delta IP_v$ vs. $\delta\Delta IP_v$
n	8	5
Intercept	0.03	−0.01
Slope	0.66	0.66
SD of intercept	0.02	0.05
SD of slope	0.05	0.13
SD of regression	0.04	0.09
r	0.98	0.95
NH: intercept = 0	CL < 0.95	CL < 0.95
NH: slope = 0	CL > 0.999	0.95 < CL < 0.99
NH: slope = 1	CL > 0.999	CL < 0.95
NH: $r = 0$	CL > 0.999	0.95 < CL < 0.99

[a] For meaning of symbols, see footnote to Table 2.

On the contrary, the $\delta\Delta IP_v$ (anilines) vs. $\delta\Delta IP_v$ (indoles) correlation displays the same slope value (0.66) but an uncertain significance (Table 7) and therefore a different mechanism of reaction for the two series in the gas phase.

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