# STATISTICAL STUDY OF THE INFLUENCE OF THE NITRO GROUPS ON THE IONIZATION AND SOLVATION PROCESSES OF DISUBSTITUTED BENZOIC DERIVATIVES

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## ABSTRACT

The influence of nitro groups on the ionization and solvation processes of disubstituted benzoic derivatives was studied from the statistical viewpoint. This study was carried out by considering the enthalpy values of these processes to be a linear combination of the enthalpy values of the same processes in the corresponding mononitrosubstituted compounds. A range of mole fractions (0–0.8) of water–DMSO mixtures was used. Diparametric and monoparametric regression analyses were carried out. In these analyses, total standard deviations, slope and intercept standard deviations, correlation coefficients, Student $t$-tests and $F$-tests of the above values were taken into account. Particular attention was paid to the presence of the collinearity between the explanatory variables. The introduction of a nitro group in position 4 both for the 3,4- and 2,4-dinitro derivatives is the dominant factor of the corresponding ionization processes.

## INTRODUCTION

The influence of the hydroxyl groups in disubstituted benzoic derivatives on the ionization and solvation processes has recently been studied in our laboratory [1]. This study was carried out from the statistical viewpoint by using monoparametric and diparametric regression analyses in order to ascertain in which benzene ring positions the influence of the hydroxyl groups plays a major role.

DMSO–water mixtures, whose dielectric constants change in a continuous way, were used as the reaction media. It was thus possible to observe the variation in the strength of the acid as a function of the solvation of the ions and undissociated molecules. It is well known that statistical analysis is able to supply useful methods for revealing small variations in structure of the

skeleton of a molecule, as a result of the introduction of the same groups in different positions [2–7]. However, there is a distinct possibility of incorrectly using the results obtained, resulting in misleading conclusions. In particular, for diparametric linear regression, special attention must be paid to the so-called collinearity, i.e. the presence of correlations between one independent (explanatory) variable and another. In this context [1] it was useful to apply a monoparametric regression analysis as well. With these two analyses it was possible to supply a complete picture of the reciprocal influence of the hydroxyl groups in the various benzene ring positions.

This work aims at studying the reciprocal influence of the nitro groups in positions 2, 3, 4 and 5 and compares these effects with those of the dihydroxy derivatives previously studied [1].

EXPERIMENTAL AND PROCEDURE

The calorimetric measurements were performed using a Tronac 450 calorimeter and an L.K.B. reaction and solution calorimeter. The calorimetric measurements were read using a Basic program running on an Olivetti M24 computer [8,9].

DMSO (Erba, RP) was purified according to the procedure of Synnot and Butler [10]. DMSO–water mixtures were prepared by weighing purified DMSO and $CO_2$-free, double-distilled water. The mole fraction of DMSO in these mixtures ranged from 0.0 to 0.8. An aqueous solution of 0.099 M NaOH and solutions of 0.99 M HCl in various DMSO–water mixtures were prepared from standard solutions and their concentrations were checked by potentiometric titrations. 2,4-, 3,4- and 3,5-dinitro benzoic acids (Fluka) were purified by crystallization from water–ether mixtures and their melting points were checked before use.

The dinitrobenzoic sodium salt solutions were prepared by adding NaOH solutions of known molarity to dinitrobenzoic acids dissolved in the DMSO–water mixtures. As a result, 100 g of DMSO–water solution at $X$ mole fraction were obtained. The concentration of the sodium salt was always in the range $2 \times 10^{-3}$–$4 \times 10^{-3}$ M.

A certain amount of acid (about 4–5% of the original content) was not converted into the salt and remained as free acid to avoid the presence of free alkali.

The ionization process of $Y, Z(NO_2)_2 PhCOOH$ (where $Y, Z$ are the pairs of numbers 2,4; 3,4; 3,5 in the various $H_2O$–DMSO mixtures can be represented as

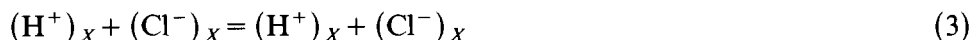$$[Y, Z(NO_2)_2 PhCOOH]_X \rightarrow [Y, Z(NO_2)_2 PhCOO^-]_X + (H^+)_X \qquad (1)$$
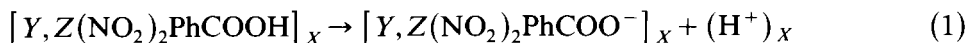
The partial molar enthalpy of ionization $\Delta \overline{H}_1$ of $Y, Z(NO_2)_2 PhCOOH$ acid was obtained by experimental measurements of the following.

(a) The partial molar enthalpy of reaction $\Delta \overline{H}_2$ of $Y,Z(NO_2)_2PhCOONa$ dissolved in the mixed solvent of $X$ mole fraction, with 0.99 M HCl also dissolved in $X$ mole fraction

$$[Y,Z(NO_2)_2PhCOO^-]_X + (Na^+)_X + (H^+)_X + (Cl^-)_X$$
$$= [Y,Z(NO_2)_2PhCOOH]_X + (Na^+)_X + (Cl^-)_X \tag{2}$$
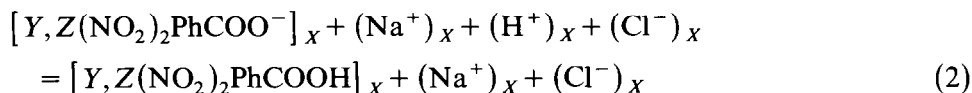
(b) The partial molar enthalpy of dilution $\Delta \overline{H}_3$ of the same amount of 0.99 M HCl (dissolved in $X$ mole fraction)

$$(H^+)_X + (Cl^-)_X = (H^+)_X + (Cl^-)_X \tag{3}$$

The partial molar enthalpy of process (1) can be obtained by subtracting $\Delta \overline{H}_2$ from $\Delta \overline{H}_1$. For each of the water–DMSO mixtures at $X$ mole fraction, the $\Delta \overline{H}_1$ refer to the ionization process of one mole of $Y,Z(NO_2)_2PhCOOH$ dissolved at infinite dilution in 1000 g of mixed solvent, yielding one mole of protons and one mole of $Y,Z(NO_2)_2PhCOO^-$ ions solvated in the same amount of solvent.

In order to refer process (1) to an initial thermodynamic state only, the solution enthalpies of crystalline $Y,Z(NO_2)_2PhCOOH$ $\Delta \overline{H}_s$ in the various solvent mixtures were measured

$$Y,Z(NO_2)_2PhCOOH_{(Cry.)} \rightarrow [Y,Z(NO_2)_2PhCOOH]_X \tag{4}$$
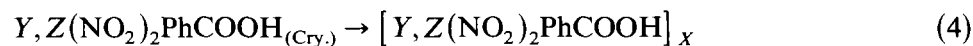
so that $\Delta \overline{H}_5 = \Delta \overline{H}_4 + \Delta \overline{H}_1$ values obtained for the process

$$Y,Z(NO_2)_2PhCOOH_{(Cry.)} \rightarrow [Y,Z(NO_2)_2PhCOO^-]_X + (H^+)_X \tag{5}$$
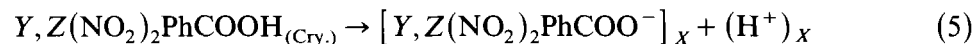
refer to an identical initial thermodynamic state. In processes (2) and (4) concentrations ranging from $2 \times 10^{-3}$ to $4 \times 10^{-3}$ M were used. Therefore, the $\Delta \overline{H}$ values related to these processes were assumed to be equal to $\Delta H^{\ominus}$ values [11].

A program which supplies monoparametric and diparametric linear regression equations, with total standard deviation, slope and intercept standard deviations, and correlation coefficients for all the above values was run on an Olivetti M24 computer.

Moreover, for monoparametric and diparametric regression equations the following null hypotheses were considered: (1) for the slope of monoparametric, $b = 0$; (2) for the slopes of diparametric, $b_1 = 0$ and $b_2 = 0$. The null hypotheses were tested by using the Student $t$-test. The $t$ values of $b$, $b_1$ and $b_2$ were calculated by means of the expressions $t_b = (b - B)/S_b$ and $t_j = (b_j - B)/S_{b_j}$, where $B = 0$ and $S_b$ and $S_{b_j}$ are the standard deviations of $b$, and $b_1$ and $b_2$, respectively and were compared with those of a set of $t$-tables. If $t > t_{CL,n-2}$ or $t > t_{CL,n-3}$ where $n - 2$ and $n - 3$ are the degrees of freedom of the system and CL is the confidence level for the significance of the regression, then for CL < 0.95 the null hypothesis is accepted (chemical hypothesis) while for CL > 0.999 its rejection is highly significant. The goodness of the diparametric fit was tested by means of an $F$-test. The $F$

values were calculated from the expressions $F = r^2(n - 3)/2(1 - r^2)$ and were compared with those of $F_{CL,n-3}$ tables (where $n - 3$ is the degree of freedom and CL the confidence level). If $F > F_{CL,n-3}$, at CL > 0.999, then the goodness of the fit is highly significant.

Moreover, for the diparametric regression, a comparison between $b_1$ and $b_2$ parameters, after their "standardization" [2,7] by means of the equations

$$b_1' = |b_1| \left[ \Sigma(x_1 - \bar{x}_1)^2 / \Sigma(y_1 - \bar{y}_1)^2 \right]^{1/2}$$

$$b_2' = |b_2| \left[ \Sigma(x_2 - \bar{x}_2)^2 / \Sigma(y_2 - \bar{y}_2)^2 \right]^{1/2}$$

allows us to calculate the percentage of correlation between $x$ or $x$ with $y$. The effect of collinearity is to increase the standard errors of the regression coefficients $b_1$ and $b_2$.

RESULTS AND DISCUSSION

Tables 1–3 show $\Delta H^{\ominus}$ values of processes (1), (4) and (5) for the 2,4-, 3,4- and 3,5-dinitro substituted benzoic acids. For the sake of comparison, it is convenient to express the ionization enthalpy values $\Delta H_1^{\ominus}$, as the difference between the values obtained in the mixed solvent at $X$ mole fraction and those in pure water, so that $\delta \Delta H_1^{\ominus} = (\Delta H_1^{\ominus})_X - (\Delta H_1^{\ominus})_{X=0}$. These values represent the transfer of the ionization process, while the $\delta \Delta H_4^{\ominus}$ and $\delta \Delta H_5^{\ominus}$ values represent the transfer enthalpy of the undissociated molecules and of the two ions $H^+$ and $Y, Z(NO_2)_2 PhCOO^-$, respectively, from pure water to mixed solvent. $\delta \Delta H_1^{\ominus}$ and $\delta \Delta H_5^{\ominus}$ also represent the solvation of the molecules and ions, at the various mole fractions, with respect to the pure water.

TABLE 1

Enthalpy values (kcal mol$^{-1}$) of processes (1), (4) and (5) for 2,4-dinitrobenzoic acid in water–DMSO mixtures of various mole fraction at 25°C

| $X$ (DMSO) | $\Delta H_1^{\ominus}$ | $\Delta H_4^{\ominus}$ | $\Delta H_5^{\ominus}$ |
|---|---|---|---|
| 0.0 | −0.22 | 4.01 | 3.79 |
| 0.1 | −0.53 | 5.83 | 5.30 |
| 0.2 | −0.84 | 5.71 | 4.87 |
| 0.3 | −0.55 | 5.03 | 4.48 |
| 0.4 | 0.49 | 3.12 | 3.61 |
| 0.5 | 1.29 | 1.80 | 3.09 |
| 0.6 | 1.63 | 1.31 | 2.94 |
| 0.7 | 3.31 | 0.28 | 3.59 |
| 0.8 | 3.23 | −0.61 | 2.62 |

TABLE 2

Enthalpy values (kcal mol$^{-1}$) of processes (1), (4) and (5) for 3,4-dinitrobenzoic acid in water–DMSO mixtures of various mole fraction at 25°C

| X (DMSO) | $\Delta H_1^{\ominus}$ | $\Delta H_4^{\ominus}$ | $\Delta H_5^{\ominus}$ |
|---|---|---|---|
| 0.0 | 0.33 | 6.73 | 7.06 |
| 0.1 | 0.37 | 6.37 | 6.74 |
| 0.2 | 0.16 | 5.75 | 5.91 |
| 0.3 | 1.03 | 6.03 | 7.06 |
| 0.4 | 1.53 | 2.55 | 4.08 |
| 0.5 | 2.14 | 2.64 | 4.78 |
| 0.6 | 3.24 | 1.26 | 4.50 |
| 0.7 | 3.82 | 0.75 | 4.57 |
| 0.8 | 4.43 | 0.25 | 4.68 |

A calorimetric acidity scale can be given and explained as a function of the different positions of the nitro groups in the benzene ring. The order based on the ionization enthalpies (Tables 1–3) is 2,4(NO$_2$)$_2$PhCOOH > 3,4(NO$_2$)$_2$PhCOOH > 3,5(NO$_2$)$_2$PhCOOH. 2,4(NO$_2$)$_2$PhCOOH is the strongest acid.

This can be explained taking into account the solvation values of the ions and of the undissociated molecules of the three nitro derivatives (Tables 4–6). From these values the following scale of solvation for the undissociated molecules can be inferred: 3,5(NO$_2$)$_2$PhCOOH > 3,4(NO$_2$)$_2$PhCOOH > 2,4(NO$_2$)$_2$PhCOOH. For the ions (Tables 4–6) the scale of solvation shows the following order: 3,4(NO$_2$)$_2$PhCOO$^-$ > 2,4(NO$_2$)$_2$PhCOO$^-$ > 3,5(NO$_2$)$_2$PhCOO$^-$. From this picture it seems, as is to be expected, that the solvation term of the undissociated molecules is more important than the solvation term of the ions.

TABLE 3

Enthalpy values (kcal mol$^{-1}$) of processes (1), (4) and (5) for 3,5-dinitrobenzoic acid in water–DMSO mixtures of various mole fraction at 25°C

| X (DMSO) | $\Delta H_1^{\ominus}$ | $\Delta H_4^{\ominus}$ | $\Delta H_5^{\ominus}$ |
|---|---|---|---|
| 0.0 | −0.22 | 8.11 | 7.89 |
| 0.1 | 0.90 | 6.46 | 7.36 |
| 0.2 | 1.99 | 6.85 | 8.84 |
| 0.3 | 3.63 | 6.39 | 10.02 |
| 0.4 | 5.51 | 5.38 | 10.89 |
| 0.5 | 7.33 | 4.12 | 11.45 |
| 0.6 | 8.77 | 2.39 | 11.70 |
| 0.7 | 9.50 | 2.11 | 11.64 |
| 0.8 | 9.30 | 1.96 | 12.26 |

## TABLE 4

Enthalpy for the transfer of the ionization process ($\delta \Delta H_1^{\ominus}$); transfer enthalpies of the undissociated molecules ($\delta \Delta H_4^{\ominus}$) and of the ions ($\delta \Delta H_5^{\ominus}$) of 2,4-dinitrobenzoic acid from pure water to solvent mixtures

| X (DMSO) | $\delta \Delta H_1^{\ominus}$ | $\delta \Delta H_4^{\ominus}$ | $\delta \Delta H_5^{\ominus}$ |
|---|---|---|---|
| 0.1 | $-0.31$ | 1.82 | 1.51 |
| 0.2 | $-0.62$ | 1.70 | 1.08 |
| 0.3 | $-0.33$ | 1.02 | 0.69 |
| 0.4 | 0.71 | $-0.89$ | $-0.18$ |
| 0.5 | 1.51 | $-2.21$ | $-0.70$ |
| 0.6 | 1.85 | $-2.70$ | $-0.85$ |
| 0.7 | 3.53 | $-3.73$ | $-0.20$ |
| 0.8 | 3.45 | $-4.62$ | $-1.17$ |

## TABLE 5

Enthalpy for the transfer of the ionization process ($\delta \Delta H_1^{\ominus}$); transfer enthalpies of the undissociated molecules ($\delta \Delta H_4^{\ominus}$) and of the ions ($\delta \Delta H_5^{\ominus}$) of 3,4-dinitrobenzoic acid from pure water to solvent mixtures

| X (DMSO) | $\delta \Delta H_1^{\ominus}$ | $\delta \Delta H_4^{\ominus}$ | $\delta \Delta H_5^{\ominus}$ |
|---|---|---|---|
| 0.1 | 0.04 | $-0.36$ | $-0.32$ |
| 0.2 | $-0.17$ | $-0.98$ | $-1.15$ |
| 0.3 | 0.70 | $-0.70$ | 0.00 |
| 0.4 | 1.20 | $-4.18$ | $-2.98$ |
| 0.5 | 1.81 | $-4.09$ | $-2.28$ |
| 0.6 | 2.91 | $-5.47$ | $-2.56$ |
| 0.7 | 3.49 | $-5.98$ | $-2.49$ |
| 0.8 | 4.10 | $-6.48$ | $-2.38$ |

## TABLE 6

Enthalpy for the transfer of the ionization ($\delta \Delta H_1^{\ominus}$); transfer enthalpies of the undissociated molecules ($\delta \Delta H_4^{\ominus}$) and of the ions ($\delta \Delta H_5^{\ominus}$) of 3,5-dinitrobenzoic acid from pure water to solvent mixtures

| X (DMSO) | $\delta \Delta H_1^{\ominus}$ | $\delta \Delta H_4^{\ominus}$ | $\delta \Delta H_5^{\ominus}$ |
|---|---|---|---|
| 0.1 | 1.12 | $-1.65$ | $-0.53$ |
| 0.2 | 2.21 | $-1.26$ | 0.95 |
| 0.3 | 3.85 | $-1.72$ | 2.13 |
| 0.4 | 5.73 | $-2.73$ | 3.00 |
| 0.5 | 7.55 | $-3.29$ | 3.56 |
| 0.6 | 8.99 | $-5.72$ | 3.81 |
| 0.7 | 9.72 | $-6.00$ | 3.75 |
| 0.8 | 9.52 | $-6.15$ | 4.37 |

As previously shown [1], statistical analysis is able to supply useful methods for comparing and explaining the substituent effects in the benzene ring in terms of probability.

In order to better understand the contributions of each of the two nitro groups on the ionization and solvation processes for the 3,4- and 2,4-dinitro derivatives, it is possible to consider the enthalpy values of these processes as a linear combination of those enthalpy values related to the same processes occurring in 2-, 3- and 4-mononitro derivatives over the whole mole fraction range.

Using a linear diparametric regression between the enthalpy values of 3,4- and 2,4-dinitro derivatives and 2-, 3- and 4-mononitro derivatives, for the ionization and solvation processes, one obtains the equation $y = a + b_1 x_1 + b_2 x_2$ where, for example, $y = \Delta H_{3,4NO_2}$, $x_1 = \Delta H_{3NO_2}$, $x_2 = \Delta H_{4NO_2}$, $a$ is the intercept and $b_1$ and $b_2$ the slopes. This diparametric equation, together with the two corresponding monoparametric equations ($\Delta H_{3,4NO_2}$ vs. $\Delta H_{3NO_2}$ and $\Delta H_{3,4NO_2}$ vs. $\Delta H_{4NO_2}$) and the regression between the explanatory variables $\Delta H_{3NO_2}$ vs. $\Delta H_{4NO_2}$ (collinearity regression), gives a good picture of the effects of nitro groups in the positions 2, 3 and 4 for the above processes.

### 3,4-Dinitrosubstituted derivative

#### Ionization process

The values obtained for the diparametric regression equation are given in Table 7. The large value of the standard deviation of the coefficient $b_1$ of $\Delta H_{3NO_2}$ rules out this term. The standard deviation of the coefficient $b_2$ of the $\Delta H_{4NO_2}$ term is acceptable. According to this, both the monoparametric regressions $\Delta H_{3,4NO_2}$ vs. $\Delta H_{3NO_2}$ and $\Delta H_{3NO_2}$ vs. $\Delta H_{4NO_2}$ (explanatory

TABLE 7

Results of the diparametric regression analysis of the ionization process of 3,4-dinitrobenzoic acid as a function of the ionization processes of the 3- and 4-nitrobenzoic derivatives

| | |
|---|---|
| $n$ | 9 |
| $a$ | −0.06 |
| $b_1$ | 0.01 |
| $b_2$ | 0.28 |
| SD $(a)$ | 0.49 |
| SD $(b_1)$ | 0.06 |
| SD $(b_2)$ | 0.07 |
| SD of regression | 0.70 |
| $r$ | 0.93 |
| $F^\star$ | 17.94 |
| n.h.: $b_1 = 0$ | CL < 0.95 |
| n.h.: $b_2 = 0$ | 0.99 < CL < 0.999 |

$F^\star > F_{CL,2,n-3}$ at CL = 0.99.

TABLE 8

Results of the monoparametric regression analysis of the ionization process of 3,4-dinitro-benzoic acid as a function of the ionization processes of the 3- and 4-nitrobenzoic derivatives

|  | $\Delta H_{3,4}$ vs. $\Delta H_3$ | $\Delta H_{3,4}$ vs. $\Delta H_4$ | $\Delta H_3$ vs. $\Delta H_4$ |
|---|---|---|---|
| $n$ | 8 | 8 | 8 |
| Intercept | −0.07 | 0.10 | 4.92 |
| Slope | 0.20 | 0.30 | 0.82 |
| SD of intercept | 0.84 | 0.41 | 2.50 |
| SD of slope | 0.07 | 0.52 | 0.32 |
| SD of regression | 1.21 | 0.73 | 4.47 |
| $r$ | 0.72 | 0.91 | 0.70 |
| n.h.: slope = 0 | 0.95 < CL < 0.99 | CL > 0.999 | 0.95 < CL < 0.99 |

$n$, number of points; SD, standard deviation; $r$, correlation coefficient; n.h., null hypothesis; CL, confidence level.

variables) are uncertain, while the regression $\Delta H_{3,4NO_2}$ vs. $\Delta H_{4NO_2}$ is highly significant (Table 8). This it can be hypothesized that the effect of the nitro group in position 4 is dominant.

### Solvation process of undissociated molecules

The values obtained for the diparametric regression equation are given in Table 9. The large values of the standard deviations on the $b_1$ and $b_2$ coefficients of $\Delta H_{3NO_2}$ and $\Delta H_{4NO_2}$ are due to the high degree of association between the explanatory variables. Indeed the monoparametric linear regressions $\Delta H_{3NO_2}$ vs. $\Delta H_{4NO_2}$, $\Delta H_{3,4NO_2}$ vs. $\Delta H_{3NO_2}$ and $\Delta H_{3,4NO_2}$ vs. $\Delta H_{4NO_2}$

TABLE 9

Results of the diparametric regression analysis of the solvation process of the undissociated molecules of 3,4-dinitrobenzoic acid as a function of the solvation processes of the undissociated molecules of the 3- and 4-nitrobenzoic derivatives

| | |
|---|---|
| $n$ | 8 |
| $a$ | 5.60 |
| $b_1$ | 0.75 |
| $b_2$ | 1.51 |
| SD $(a)$ | 5.79 |
| SD $(b_1)$ | 0.28 |
| SD $(b_2)$ | 1.13 |
| SD of regression | 0.65 |
| $r$ | 0.98 |
| $F^\star$ | 49.84 |
| n.h.: $b_1 = 0$ | 0.95 < CL < 0.99 |
| n.h.: $b_2 = 0$ | CL < 0.95 |

$F^\star > F_{CL,2,n-3}$ at CL = 0.999.

TABLE 10

Results of the monoparametric regression analysis of the solvation process of the undissociated molecules of 3,4-dinitrobenzoic acid as a function of the solvation processes of the undissociated molecules of the 3- and 4-nitrobenzoic derivatives

|  | $\Delta H_{3,4}$ vs. $\Delta H_3$ | $\Delta H_{3,4}$ vs. $\Delta H_4$ | $\Delta H_3$ vs. $\Delta H_4$ |
|---|---|---|---|
| $n$ | 8 | 8 | 8 |
| Intercept | $-2.13$ | 19.49 | 18.60 |
| Slope | 1.10 | 4.25 | 3.67 |
| SD of intercept | 0.29 | 3.39 | 3.45 |
| SD of slope | 0.12 | 0.62 | 0.63 |
| SD of regression | 0.69 | 0.91 | 0.93 |
| $r$ | 0.97 | 0.94 | 0.92 |
| n.h.: slope $= 0$ | CL $> 0.999$ | CL $> 0.999$ | CL $> 0.999$ |

$n$, number of points; SD, standard deviation; $r$, correlation coefficient; n.h., null hypothesis; CL, confidence level.

are highly significant (Table 10). Thus the contributions of the 3-$NO_2PhCOOH$ and 4-$NO_2PhCOOH$ on the ionization process of the $3,4(NO_2)_2PhCOOH$ cannot be compared.

### Solvation process of ions

The diparametric (Table 11) and the corresponding three monoparametric (Table 12) linear regressions are all insignificant.

From this evidence it can be inferred that the nitro group in position 4

TABLE 11

Results of the diparametric regression analysis of the solvation process of the ions of 3,4-dinitrobenzoic acid as a function of the solvation processes of the ions of the 3- and 4-nitrobenzoic derivatives

| $n$ | 8 |
|---|---|
| $a$ | $-0.68$ |
| $b_1$ | $-0.10$ |
| $b_2$ | $-0.14$ |
| SD $(a)$ | 0.89 |
| SD $(b_1)$ | 0.09 |
| SD $(b_2)$ | 0.07 |
| SD of regression | 0.82 |
| $r$ | 0.78 |
| $F^\star$ | 4.01 |
| n.h.: $b_1 = 0$ | CL $< 0.95$ |
| n.h.: $b_2 = 0$ | CL $< 0.95$ |

$F^\star > F_{CL,2,n-3}$ at CL $< 0.95$.

TABLE 12

Results of the monoparametric regression analysis of the solvation process of the ions of 3,4-dinitrobenzoic acid as a function of the solvation processes of the ions of the 3- and 4-nitrobenzoic derivatives

| | $\Delta H_{3,4}$ vs. $\Delta H_3$ | $\Delta H_{3,4}$ vs. $\Delta H_4$ | $\Delta H_3$ vs. $\Delta H_4$ |
|---|---|---|---|
| $n$ | 8 | 8 | 8 |
| Intercept | $-0.19$ | $-1.69$ | 9.51 |
| Slope | $-0.16$ | $-0.16$ | 0.25 |
| SD of intercept | 1.07 | 0.30 | 1.35 |
| SD of slope | 0.10 | 0.07 | 0.29 |
| SD of regression | 1.02 | 0.85 | 3.79 |
| $r$ | 0.54 | 0.71 | 0.32 |
| n.h.: slope = 0 | CL < 0.95 | 0.95 < CL < 0.99 | CL < 0.95 |

$n$, number of points; SD, standard deviation; $r$, correlation coefficient; n.h., null hypothesis; CL, confidence level.

plays a major role in the ionization process. However, the dominant solvation process cannot be distinguished.

## 2,4-Dinitrosubstituted derivative

### Ionization process
The diparametric equation is insignificant (Table 13), while the corresponding monoparametric equations are significant (Table 14). Thus it is not possible to compare the influence of $\Delta H_{2NO_2}$ and $\Delta H_{4NO_2}$ on the $\Delta H_{2,4NO_2}$.

### Solvation process of undissociated molecules
The diparametric regression displays a good fit (Table 15). The standard

TABLE 13

Results of the diparametric regression analysis of the ionization process 2,4-dinitrobenzoic acid as a function of the ionization processes of the 2- and 4-nitrobenzoic derivatives

| | |
|---|---|
| $n$ | 9 |
| $a$ | $-0.93$ |
| $b_1$ | 0.09 |
| $b_2$ | 0.21 |
| SD $(a)$ | 0.52 |
| SD $(b_1)$ | 0.14 |
| SD $(b_2)$ | 0.11 |
| SD of regression | 0.92 |
| $r$ | 0.87 |
| $F^\star$ | 9.5 |
| n.h.: $b_1 = 0$ | CL < 0.95 |
| n.h.: $b_2 = 0$ | CL < 0.95 |

$F^\star > F_{CL.2.n-3}$ at CL < 0.95.

TABLE 14

Results of the monoparametric regression analysis of the ionization process of 2,4-dinitro-benzoic acid as a function of the ionization processes of the 2- and 4-nitrobenzoic derivatives

| | $\Delta H_{3,4}$ vs. $\Delta H_3$ | $\Delta H_{3,4}$ vs. $\Delta H_4$ | $\Delta H_3$ vs. $\Delta H_4$ |
|---|---|---|---|
| $n$ | 9 | 9 | 9 |
| Intercept | $-0.66$ | $-0.81$ | 0.58 |
| Slope | 0.31 | 0.27 | 0.69 |
| SD of intercept | 0.56 | 0.49 | 1.35 |
| SD of slope | 0.09 | 0.06 | 0.17 |
| SD of regression | 1.04 | 0.88 | 2.41 |
| $r$ | 0.79 | 0.86 | 0.84 |
| n.h.: slope $= 0$ | $0.99 < CL < 0.999$ | $0.99 < CL < 0.999$ | $0.99 < CL < 0.999$ |

$n$, number of points; SD, standard deviation; $r$, correlation coefficient; n.h., null hypothesis; CL, confidence level.

deviation of the $\Delta H_{2NO_2}$ coefficient ($b_1$) is acceptable while that of the $\Delta H_{4NO_2}$ coefficient is very large. The high significance of the three mono-parametric regressions indicates that $b_1$ and $b_2$ cannot be compared (Table 16).

*Solvation process of ions*

The diparametric regression shows a good fit (Table 17). The standard deviation of the $b_2$ coefficient of $\Delta H_{4NO_2}$ is acceptable. The monoparametric series (Table 18) shows that $\Delta H_{2,4NO_2}$ vs. $\Delta H_{4NO_2}$ is significant, $\Delta H_{2NO_2}$ vs. $\Delta H_{4NO_2}$ (explanatory variables) is insignificant and $\Delta H_{2,4NO_2}$ vs. $\Delta H_{2NO_2}$ is uncertain.

TABLE 15

Results of the diparametric regression analysis of the solvation process of the undissociated molecules of 2,4-dinitrobenzoic acid as a function of the solvation processes of the undissociated molecules of the 2- and 4-nitrobenzoic derivatives

| | |
|---|---|
| $n$ | 8 |
| $a$ | 2.28 |
| $b_1$ | 0.80 |
| $b_2$ | 0.49 |
| SD $(a)$ | 1.41 |
| SD $(b_1)$ | 0.12 |
| SD $(b_2)$ | 0.30 |
| SD of regression | 0.83 |
| $r$ | 0.96 |
| $F^\star$ | 28.75 |
| n.h.: $b_1 = 0$ | $0.99 < CL < 0.999$ |
| n.h.: $b_2 = 0$ | $CL < 0.95$ |

$F^\star > F_{CL,2,n-3}$ at $CL = 0.99$.

TABLE 16

Results of the monoparametric regression analysis of the solvation process of the undissociated molecules of 2,4-dinitrobenzoic acid as a function of the solvation processes of the undissociated molecules of the 2- and 4-nitrobenzoic derivatives

|  | $\Delta H_{2,4}$ vs. $\Delta H_2$ | $\Delta H_{2,4}$ vs. $\Delta H_4$ | $\Delta H_2$ vs. $\Delta H_4$ |
|---|---|---|---|
| $n$ | 8 | 8 | 8 |
| Intercept | 0.39 | 22.00 | 19.38 |
| Slope | 1.10 | 4.30 | 3.88 |
| SD of intercept | 0.27 | 3.40 | 2.89 |
| SD of slope | 0.08 | 0.62 | 0.52 |
| SD of regression | 0.50 | 0.91 | 0.77 |
| $r$ | 0.98 | 0.94 | 0.95 |
| n.h.: slope = 0 | CL > 0.999 | CL > 0.999 | CL > 0.999 |

$n$, number of points; SD, standard deviation; $r$, correlation coefficient; n.h., null hypothesis; CL, confidence level.

TABLE 17

Results of the diparametric regression analysis of the solvation process of the ions of 2,4-dinitrobenzoic acid as a function of the solvation processes of the ions of the 2- and 4-nitrobenzoic derivatives

| $n$ | 8 |
|---|---|
| $a$ | 1.10 |
| $b_1$ | $-0.20$ |
| $b_2$ | $-0.13$ |
| SD $(a)$ | 0.49 |
| SD $(b_1)$ | 0.09 |
| SD $(b_2)$ | 0.04 |
| SD of regression | 0.39 |
| $r$ | 0.94 |
| $F^\star$ | 19.04 |
| n.h.: $b_1 = 0$ | CL < 0.95 |
| n.h.: $b_2 = 0$ | 0.99 < CL < 0.999 |

$F^\star > F_{CL,2,n-3}$ at CL = 0.99.

TABLE 18

Results of the monoparametric regression analysis of the solvation process of the ions of 2,4-dinitrobenzoic acid as a function of the solvation processes of the ions of the 2- and 4-nitrobenzoic derivatives

|  | $\Delta H_{2,4}$ vs. $\Delta H_2$ | $\Delta H_{2,4}$ vs. $\Delta H_4$ | $\Delta H_2$ vs. $\Delta H_4$ |
|---|---|---|---|
| $n$ | 8 | 8 | 8 |
| Intercept | 2.01 | 0.12 | 4.92 |
| Slope | $-0.39$ | $-0.17$ | 0.22 |
| SD of intercept | 0.72 | 0.12 | 0.59 |
| SD of slope | 0.13 | 0.04 | 0.13 |
| SD of regression | 0.65 | 0.49 | 1.67 |
| $r$ | 0.76 | 0.88 | 0.60 |
| n.h.: slope = 0 | 0.95 < CL < 0.99 | 0.99 < CL < 0.999 | CL < 0.95 |

$n$, number of points; SD, standard deviation; $r$, correlation coefficient; n.h., null hypothesis; CL, confidence level.

TABLE 19

Results of the monoparametric regression analysis of the ionization process for 3,4-dinitro-benzoic acid as a function of the ionization processes of the 3,4-dihydroxy derivative

| $n$ | 9 |
|---|---|
| Intercept | $-0.20$ |
| Slope | 0.53 |
| SD of intercept | 0.21 |
| SD of slope | 0.04 |
| SD of regression | 0.37 |
| $r$ | 0.98 |
| n.h.: slope $= 0$ | CL $> 0.999$ |

Once again the nitro group in the position 4 displays a dominant effect. In addition, for the 2,4-dinitro derivative, it is possible to distinguish which of the two solvation processes is most important. This was not possible for the 3,4-dinitrobenzoic acid.

*Nitro and hydroxy disubstituted benzoic derivatives*

Finally, a statistical comparison between nitro and hydroxy [1] disubstituted benzoic derivatives (with substituent groups in the same positions) can give a deeper insight into the ionization processes of the disubstituted benzene derivatives.

*Ionization processes*
The monoparametric linear equations are highly significant for the couples 3,4-$NO_2$/OH (Table 19) and 2,4-$NO_2$/OH (Table 20).

*Solvation processes of undissociated molecules*
The monoparametric linear equations are highly significant both for the couples 3,4-$NO_2$/OH (Table 21) and 2,4-$NO_2$/OH (Table 22).

TABLE 20

Results of the monoparametric regression analysis of the ionization process for 2,4-dinitro-benzoic acid as a function of the ionization processes of the 2,4-dihydroxy derivative

| $n$ | 9 |
|---|---|
| Intercept | $-1.25$ |
| Slope | 1.29 |
| SD of intercept | 0.29 |
| SD of slope | 0.14 |
| SD of regression | 0.49 |
| $r$ | 0.96 |
| n.h.: slope $= 0$ | CL $> 0.999$ |

*Solvation processes of ions*

For these processes the monoparametric regression for the couple 2,4-$NO_2$/OH (Table 23) is insignificant and for the couple 3,4-$NO_2$/OH the

TABLE 21

Results of the monoparametric regression analysis of the solvation process of the undissociated molecules of 3,4-dinitrobenzoic acid as a function of the solvation process of the undissociated molecules of the 3,4-dihydroxy derivative

| | |
|---|---|
| *n* | 8 |
| Intercept | 0.67 |
| Slope | 0.64 |
| SD of intercept | 0.65 |
| SD of slope | 0.09 |
| SD of regression | 0.85 |
| *r* | 0.95 |
| n.h.: slope = 0 | CL > 0.999 |

TABLE 22

Results of the monoparametric regression analysis of the solvation process of the undissociated molecules of 2,4-dinitrobenzoic acid as a function of the solvation process of the undissociated molecules of the 2,4-dihydroxy derivative

| | |
|---|---|
| *n* | 9 |
| Intercept | 2.80 |
| Slope | 0.64 |
| SD of intercept | 0.53 |
| SD of slope | 0.07 |
| SD of regression | 0.74 |
| *r* | 0.96 |
| n.h.: slope = 0 | CL > 0.999 |

TABLE 23

Results of the monoparametric regression analysis of the solvation process of the ions of 3,4-dinitrobenzoic acid as a function of the solvation process of the ions of the 3,4-dihydroxy derivative

| | |
|---|---|
| *n* | 8 |
| Intercept | − 0.49 |
| Slope | 0.44 |
| SD of intercept | 0.66 |
| SD of slope | 0.20 |
| SD of regression | 0.90 |
| *r* | 0.70 |
| n.h.: slope = 0 | CL < 0.95 |

TABLE 24

Results of the monoparametric regression analysis of the solvation process of the ions of 2,4-dinitrobenzoic acid as a function of the solvation process of the ions of the 2,4-dihydroxy derivative

| $n$ | 8 |
|---|---|
| Intercept | $-0.25$ |
| Slope | 0.32 |
| SD of intercept | 0.56 |
| SD of slope | 0.10 |
| SD of regression | 0.76 |
| $r$ | 0.78 |
| n.h.: slope $= 0$ | $0.95 < CL < 0.99$ |

regression is uncertain (Table 24). These results are in agreement with the fact that the solvation of the undissociated molecules is the key factor in the ionization processes of the disubstituted benzoic derivatives [12–16].

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