



Theoretical study of substituents effect on C–NO₂ bond strength in mono substituted nitrobenzenes



G.M. Khrapkovskii^a, D.D. Sharipov^a, A.G. Shamov^a, D.L. Egorov^a, D.V. Chachkov^{a,b}, B. Nguyen Van^a, R.V. Tsyshevsky^{a,*}

^a Kazan State Technological University, 68 K. Marks Street, 420015 Kazan, Russia

^b Kazan Branch of Joint Supercomputer Center of Russian Academy of Science, 2/31 Lobachevsky Street, 420111 Kazan, Russia

ARTICLE INFO

Article history:

Received 11 March 2013
Received in revised form 14 April 2013
Accepted 14 April 2013
Available online 25 April 2013

Keywords:

Mono substituted nitrobenzenes
Bond dissociation enthalpies
Mono substituted phenyls
Enthalpy of formation
DFT
B3LYP

ABSTRACT

Enthalpies of the C–N bond dissociation of nitrobenzene and twenty-seven mono substituted nitrobenzenes along with their formation enthalpies were calculated using different multilevel (G2, G3, G3B3, CBS-QB3) and density functional theory-based B3LYP and wB97XD techniques. The gas phase enthalpies of formation of mono substituted phenyl radicals were also calculated using these methods. The calculated values of reaction enthalpies were compared with available experimental data. We have concluded based on results of present and recent article, that B3LYP level of theory with 6-31G(d,f,p') basis sets should be proposed as the accurate method for calculating formation enthalpies of mono substituted nitrobenzenes as well as enthalpies of C–NO₂ bond scission. Based on satisfactory correlation between experimental and calculated data we proposed revision of experimental activation energy of C–NO₂ bond rupture in *o*-chloronitrobenzene, *o*- and *m*-nitrotoluene as well as *p*-nitroaniline. Enthalpies of formation of some substituted phenyl radicals were estimated using experimental enthalpies of C–NO₂ bond cleavage together with formation enthalpies of mono substituted nitrobenzenes and NO₂ moiety.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Recently we reported the ability of different quantum chemistry methods predict enthalpies of formation of twenty-seven mono substituted nitrobenzenes [1]. It was shown that the overall best agreement with experiment within atomization approach was achieved by using Gn multilevel techniques and long range corrected density functional wB97XD level of theory, whereas average absolute deviations computed for these methods did not exceed 1.6 kcal/mol. In present paper we would like to perform results of our theoretical study aiming to explore the effect of substituents on C–NO₂ bond strength in mono substituted nitrobenzenes.

Thermal decomposition of nitroaromatic compounds has received much attention as a prototypes of explosives materials due to relatively strong C–NO₂ bond [2,3] and thus effect of molecular structure on C–NO₂ bond strength in nitroaromatic compounds are of tremendous fundamental and practical importance. Although C–NO₂ bond strength in nitrobenzene with one and several substituents was the object of several theoretical studies employing DFT methods [4–8], the effect of various substituents on C–NO₂ bond strength in mono nitrobenzene has not been yet studied systematically employing different methods of quantum

chemistry techniques. According to Shao B3P86/6-311G** [6] and B3PW91/6-31G** [7] levels were found to be very accurate for calculating BDE values of some OH, NH₂ and CH₃ mono substituted nitrobenzenes, trinitrobenzene and trinitrotoluene. Nevertheless, as it was shown in [1] both of these methods produced poor agreement with experiment for enthalpies of formation of mono substituted nitrobenzenes. Therefore, accurate performance of C–NO₂ bond enthalpies is solely due to cancelling of errors accumulated in formation enthalpies of initial mono nitrobenzenes and corresponding radical moieties.

Present paper consists of two main parts. Effect of various substituents on enthalpies of C–NO₂ bond rupture in mono nitrobenzene is discussed in the first part, the second part devoted to formation enthalpies of mono substituted phenyl radicals. From our point of view such extensive theoretical study carried out with employing different DFT and composite techniques will provide better understanding of reactivity of this important class of organic compounds.

2. Materials and methods

All calculations were carried out using Gaussian 09 [9] program. In this work we used G2 [10], G3 [11], G3B3 [12] and CBS-QB3 [13,14] multilevel composite methods. Calculations at DFT [15,16] level were performed by employing adiabatically coupled B3LYP

* Corresponding author. Tel.: +7 301 405 0221.

E-mail address: roman.tsyshevsky@yahoo.com (R.V. Tsyshevsky).

[17,18] method and long range corrected wB97XD functional of Chai and Head-Gordon [19].

C–N bond dissociation enthalpies were calculated at 298 K according to the following equation:

$$\Delta_f H^0(R_1 - R_2) = [\Delta_f H_{298}(R_1) + \Delta_f H_{298}(R_2)] - \Delta_f H_{298}(R_1 - R_2), \quad (1)$$

in which $H_{298}(R_1 - R_2)$, $\Delta_f H_{298}(R_1)$ and $\Delta_f H_{298}(R_2)$ are formation enthalpies of the initial molecule and corresponding radicals respectively. Required values of formation enthalpies were obtained using atomization approach and isodesmic reactions.

The absolute deviation (AD_i) and average absolute deviation (AAD) were calculated from the following equations:

$$AD_i = |x_i - y_i| \quad (2)$$

and (4)

$$AAD = \frac{1}{n} \sum_{i=1}^n AD_i, \quad (3)$$

where x_i – calculated parameter and y_i – experimental value.

3. Results and discussion

3.1. C–NO₂ bond dissociation enthalpies

Calculated C–NO₂ bond dissociation enthalpies (BDEs) are collected in Table 1 along with experimental activation energies (E_a). We decided to include in Table 1 only most accurate BDE values predicted at B3LYP level of theory, whereas detailed discussion of availability of B3LYP level of theory with various basis sets

produce accurate enthalpies of C–NO₂ bond cleavage was performed in [20].

In the beginning of discussion we would like to notice that all quantum chemistry methods produce similar trends for influence of different substituents on enthalpies of C–NO₂ bond cleavage as it is from correlation trends depicted in Fig. 1. The values of coefficient of determination (R^2) exceeds 0.971 even for in the case of G2 composite method which produces the largest deviation between calculated and experimental C–NO₂ bond dissociation enthalpies (BDEs) Table 2.

Inspection of data collected in Table 1 indicates that experimental activation energies taken from different references are in satisfactory agreement with each other, except *para*-nitrotoluene. E_a values reported by Nazin [21] and Brill [2] are noticeably lower than those taken from [6,22] and calculated estimations. Comparison of calculated and available experimental data reveals that addition of electron donor moieties such as methyl, amino and hydroxy groups to nitrobenzene in *meta*- and *para*-positions causes increasing of C–NO₂ BDE in nitrobenzene. Such inconsistency in experimental estimations may be explained by presence of impurities, contribution of secondary reactions and heterogeneous processes to rate constant of decomposition of *m*- and *p*-nitrotoluene, as it has been discussed in our earlier paper [23].

We compiled absolute deviation values and data experimental estimations reported in [2,6,21,22], recalculated for 298 K in Table 2 to analyze ability of quantum chemistry methods predict BDE values of mono substituted nitrobenzenes.

Inspection of Table 2 reveals that B3LYP level of theory demonstrates the best agreement with available experimental data. Average absolute deviation is less 1.4 kcal/mol. Multilevel composite

Table 1

Calculated at 298 K C–NO₂ BDE values together with experimental E_a estimations [2,6,21,22] for mono substituted nitrobenzenes (kcal/mol).

Compound	B3LYP/6-31G(d,p)	B3LYP/6-31G(df,p)	B3LYP/6-31G(d'f,p')	wB97xd/6-31+G(2df,p)	G2	G3	G3B3	CBS-QB3	Exp.
C ₆ H ₅ NO ₂	70.0	69.9	69.4	73.1	80.3	76.5	76.4	77.9	69.6 ^a ; 70.7 ^b ; 68.2 ^c
<i>o</i> -F-C ₆ H ₄ -NO ₂	65.8	65.8	65.3	68.2	75.9	72.7	72.1	73.2	–
<i>m</i> -F-C ₆ H ₄ -NO ₂	68.7	68.7	68.2	71.8	79.3	75.9	75.7	76.8	–
<i>p</i> -F-C ₆ H ₄ -NO ₂	70.6	70.6	70.1	73.7	80.9	77.5	77.4	78.1	–
<i>o</i> -Cl-C ₆ H ₄ -NO ₂	62.5	62.6	62.2	66.8	75.7	72.6	72.1	72.9	67.16 ^a
<i>m</i> -Cl-C ₆ H ₄ -NO ₂	68.2	68.2	67.7	71.5	79.4	75.9	75.8	76.8	70.03 ^a
<i>p</i> -Cl-C ₆ H ₄ -NO ₂	69.6	69.6	69.2	72.9	80.5	77.0	76.9	77.9	71.7 ^a
<i>o</i> -OH-C ₆ H ₄ -NO ₂	78.1	78.0	77.2	79.2	85.8	82.2	81.9	82.2	–
<i>m</i> -OH-C ₆ H ₄ -NO ₂	69.3	69.4	68.9	72.5	80.0	76.4	75.9	76.7	71.2 ^a
<i>p</i> -OH-C ₆ H ₄ -NO ₂	72.5	72.4	71.9	75.5	82.4	78.8	78.5	79.4	–
<i>o</i> -NH ₂ -C ₆ H ₄ -NO ₂	74.5	74.5	73.9	76.7	82.7	79.0	78.6	79.4	–
<i>m</i> -NH ₂ -C ₆ H ₄ -NO ₂	70.5	70.5	70.0	73.5	81.2	79.3	76.5	77.4	71.94 ^a ; 70.5 ^b
<i>p</i> -NH ₂ -C ₆ H ₄ -NO ₂	74.3	74.4	73.7	77.1	83.5	79.9	79.5	80.5	73.61 ^a ; 72.2 ^b
<i>o</i> -CH ₃ -C ₆ H ₄ -NO ₂	67.5	67.5	67.0	70.4	78.7	75.2	74.6	75.4	70.2 ^b ; 67 ^c
<i>m</i> -CH ₃ -C ₆ H ₄ -NO ₂	70.1	70.1	69.6	73.3	80.0	76.4	76.8	77.5	67.88 ^a ; 68 ^c
<i>p</i> -CH ₃ -C ₆ H ₄ -NO ₂	71.0	71.0	70.4	74.2	81.3	77.6	77.5	78.8	65.73 ^a ; 71.4 ^b ; 68.2 ^c
<i>o</i> -COH-C ₆ H ₄ -NO ₂	63.4	63.5	63.0	67.0	75.9	72.5	72.1	72.3	–
<i>m</i> -COH-C ₆ H ₄ -NO ₂	68.6	68.5	68.1	72.0	80.0	76.6	76.4	76.9	–
<i>p</i> -COH-C ₆ H ₄ -NO ₂	67.9	67.8	67.4	71.1	79.2	75.8	75.5	76.5	–
<i>o</i> -COOH-C ₆ H ₄ -NO ₂	61.0	61.3	60.8	65.7	74.8	71.4	71.1	71.3	–
<i>m</i> -COOH-C ₆ H ₄ -NO ₂	68.8	68.8	68.3	72.0	79.8	76.4	76.3	77.0	–
<i>p</i> -COOH-C ₆ H ₄ -NO ₂	68.2	68.2	67.8	71.3	79.1	75.7	75.6	76.7	–
<i>o</i> -NO ₂ -C ₆ H ₄ -NO ₂	59.5	58.7	58.3	63.3	72.8	69.8	69.8	70.0	–
<i>m</i> -NO ₂ -C ₆ H ₄ -NO ₂	66.4	67.1	66.7	70.5	78.5	75.2	75.2	75.1	67.9 ^a ; 66.5 ^b ; 68.3 ^c
<i>p</i> -NO ₂ -C ₆ H ₄ -NO ₂	67.0	66.9	66.5	70.2	78.1	74.9	74.9	75.8	68.4 ^a ; 67.0 ^b ; 68.6 ^c
<i>o</i> -CN-C ₆ H ₄ -NO ₂	63.9	63.8	63.3	67.1	76.2	72.6	72.7	73.4	–
<i>m</i> -CN-C ₆ H ₄ -NO ₂	67.6	67.5	67.0	70.8	79.3	75.7	83.9	76.0	–
<i>p</i> -CN-C ₆ H ₄ -NO ₂	67.6	67.6	67.1	70.6	79.1	75.5	75.8	76.2	–

^a Activation energies in [21] are reported for ~700 K.

^b Data from Refs. [6,22] are reported for 298 K.

^c Temperature range in [2] for NB, *m*-DNB, *p*-DNB and *m*-NT is $T = 673$ – 753 K, for *o*-NT and *p*-NT – 1100 – 1250 K.

Download English Version:

<https://daneshyari.com/en/article/5394143>

Download Persian Version:

<https://daneshyari.com/article/5394143>

[Daneshyari.com](https://daneshyari.com)