Theoretical Study of the Decomposition Reactions in Substituted Nitrobenzenes

Guillaume Fayet,[†,‡] **Laurent Joubert,**[†] **Patricia Rotureau,**[‡] **and Carlo Adamo*,**[†]

Laboratoire d'Electrochimie et Chimie Analytique, CNRS UMR-7575, Ecole Nationale Supérieure de Chimie de Paris (ENSCP), 11 rue P. et M. Curie, F-75231 Paris Cedex 05 France, and Institut National de l'Environnement Industriel et des Risques (INERIS), Parc Technologique Alata, BP2, 60550 Verneuil-en-Halatte, France
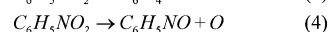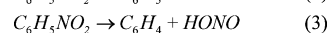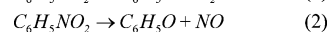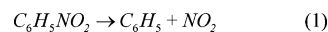
Received: January 3, 2008

The influence of substituent nature and position on the unimolecular decomposition of nitroaromatic compounds was investigated using the density functional theory at a PBE0/6-31+G(d,p) level. As the starting point, the two main reaction paths for the decomposition of nitrobenzene were analyzed: the direct carbon nitrogen dissociation ($C_6H_5 + NO_2$) and a two step mechanism leading to the formation of phenoxyl and nitro radicals ($C_6H_5O + NO$). The dissociation energy of the former reaction was calculated to be 7.5 kcal/mol lower than the activation energy of the second reaction. Then the Gibbs free energies were computed for 15 nitrobenzene derivatives characterized by different substituents (nitro, methyl, amino, carboxylic acid, and hydroxyl) in the ortho, meta, and para positions. In meta position, no significant changes appeared in the reaction energy profiles whereas ortho and para substitutions led to significant deviations in energies on the decomposition mechanisms due to the resonance effect of the nitro group without changing the competition between these mechanisms. In the case of para and meta substitutions, the carbon-nitro bond dissociation energy has been directly related to the Hammett constant as an indicator of the electron donor–acceptor effect of substituents.

1. Introduction

The lack of knowledge on the chemical properties and reactivity of energetic materials has always been the consequence of many incidents.[1,2] It is not surprising that different approaches have been developed for the full understanding and the prediction of chemical hazards, at least in simple chemical species.[3–6] The main aim of such studies was to understand the detailed mechanism of the decomposition process in order, not only to explain experimental observations, but to open new perspectives in chemical hazard prevention.[7–12] In fact, the knowledge of the (thermal) decomposition mechanisms for an explosive or potentially explosive chemical substance could guide systematic predictions about new explosive molecules, influence the feasibility of large-scale synthesis, predict long-term stability for purposes of storage, and predict sensitivity to various external stimuli, such as heat and mechanical impact.[13,14] Nevertheless, although safety (and explosive performance) is intimately connected to the decomposition mechanism, its knowledge does not automatically lead to improvement in safety and performance. However, without mechanistic information the behavior of explosives remains disconcertingly empirical.[6,15–17] This is particularly true also because experimental conditions are often dramatically different from one laboratory to another, which complicates the comparison of the data.[18]

Nitroaromatic compounds are, in particular, currently considered in the class of explosive substances,[19] and nitrobenzene is a prototypical molecule for studying the decomposition behavior of energetic materials. Among the numerous decomposition channels deeply investigated at the experimental level,[20–26] three out of the four reported in Scheme 1 are the most important. Reaction 1 and 2 are the principal decomposi-

* To whom correspondence should be addressed. E-mail: carlo-adamo@enscp.fr.
    † ENSCP.
    ‡ INERIS.

SCHEME 1

$$C_6H_5NO_2 \rightarrow C_6H_5 + NO_2 \qquad (1)$$
$$C_6H_5NO_2 \rightarrow C_6H_5O + NO \qquad (2)$$
$$C_6H_5NO_2 \rightarrow C_6H_4 + HONO \qquad (3)$$
$$C_6H_5NO_2 \rightarrow C_6H_5NO + O \qquad (4)$$

tion paths in thermal or photodissociations;[22,23,26] reaction 4 has been only observed in photodissociation, and it is negligible in thermal decomposition.[22] The same primary channels are widely indicated to be the initiation channel of decomposition for nitroaromatic compounds in the absence of ortho substituents.[27] In such last case, the decomposition reaction could be more complex, because the interaction of the NO_2 group with the ortho substituent must be considered.[8,9,28]

It must be noted that one of the paradigms in the prediction of the explosibility properties is that the weakest bond in the aromatic nitro compounds is the C–NO_2, and it is mainly responsible for the heat liberated during the explosion.[29,30]

Some theoretical studies have been devoted to the study of thermal decomposition of nitrobenzene. While a large part of such works was focused on the dissociation of the carbon–nitro-group bond,[31,32] only recently the kinetics and mechanism for the unimolecular decomposition of nitrobenzene have been deeply investigated.[7] In particular, resting on accurate electronic correlated calculation, the four reaction mechanisms of Scheme 1 have been characterized. These theoretical results suggest that reaction channels 3 and 4 could be negligible between 500 and 800 K, whereas reaction path 2 is in competition with the dissociation reaction 1. Furthermore, the reaction path 3, not experimentally observed, has been evidenced.

The relative weight of these major decomposition paths seems to be significantly determined by the substitutents to the aromatic ring. This influence has been experimentally observed, for instance, in para-substituted nitrobenzenes in a mass spectrometric analysis.[27] Also, the destabilizing effect of hydroxyl groups on nitroaromatic molecules has been investigated.[33]

Decomposition Reactions in Substituted Nitrobenzenes

J. Phys. Chem. A, Vol. 112, No. 17, 2008 **4055**
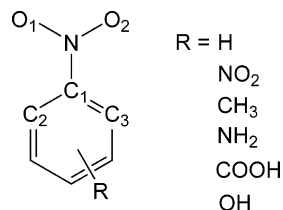
Figure 1. Sketch of the considered ortho-, meta-, and para-substituted nitrobenzenes.

In this context, we present a detailed theoretical investigation on the substituent effect on the competition between channels 1 and 2 in nitroaromatic molecules using quantum chemical methods. To this end, nitrobenzene and 15 other derivatives, obtained by changing the substituent groups (nitro, methyl, amino, carboxylic acid, and hydroxyl, shown in Figure 1) in the ortho, meta, and para positions to the nitro group, have been considered. For each of the systems, the reaction channels (1) and (2) have been analyzed through the characterization of the stationary points (reactants, transition states, and products) and the corresponding energies.

2. Computational Details

All calculations have been carried out using the Gaussian 03 package[34] and the density functional theory (DFT) both in the restricted and unrestricted Kohn−Sham approach. The parameter-free PBE0 hybrid functional[35] has been considered for all the cases. Structure optimizations were performed with a 6-31+G-(d,p) basis set and vibrational frequencies were obtained at the same level of theory. The nature of the stationary points was then checked by counting no imaginary frequency for stable species and a single for transition states. Starting from the harmonic frequencies, thermal corrections, enthalpies and Gibbs free energies have been computed using standard statistical approaches, as implemented in the Gaussian program.[34]

All calculations of the open shell molecules were performed within a spin-unrestricted formalism and spin contamination, monitored by the expectation value of S^2, was found to be negligible.

Finally, the electronic structure of these molecules has been investigated using the natural bond orbital (NBO) approach and the related natural population analysis (NPA).[36,37]

3. Results and Discussion

3.1. Reference Reaction: Nitrobenzene Decomposition. The energy variations for the two principal decomposition channels of nitrobenzene are presented in Figure 2, together with sketches of the structures of the stationary points (minima or TS). These energies, as well as enthalpies and Gibbs free energies are collected in Table 1 and have been obtained using the optimized structural parameters given in Supporting Information, Table S1.

The first reaction path is the direct breaking of the carbon−nitrogen bond, leading to the formation of the C_6H_5 and NO_2 radicals. The second reaction is characterized by a two-step mechanism: nitrobenzene ($C_6H_5NO_2$) first isomerizes to phenylnitrite (C_6H_5ONO), then the oxygen−nitrogen bond is broken to give the phenoxyl (C_6H_5O) and nitric oxide (NO) radicals. Relative Energies (ΔE) obtained with the PBE0/6-31+G(d,p) are closed to those obtained by sophisticated post-HF methods,[7] as can be seen from the data reported in Table 1. For the the second reaction channel, the activation energy corresponding to the isomerization to phenylnitrite is 63.7 kcal/mol, and phenylnitrite is 4.0 kcal/mol less stable than nitrobenzene. The

corresponding dissociation energy for the last step of this pathway (calculated as the difference between the products and the phenyl nitrite energies) is 18.5 kcal/mol, slightly higher than the 22.5 kcal/mol already reported in literature.[7] In general our results are in good agreement with those obtained with more refined ab initio calculations.[7] However, it must be noticed that the activation energies for the isomerization at phenylnitrite are lower than those needed to break the C−NO_2 bond (63.7 versus 71.2 kcal/mol). This last result is in contradiction with the experimental assumption that the heat released during the explosion is to be mainly ascribed to the last process.[29,30] In Table 1, the enthalpies and the Gibbs free energies for the two processes are also reported. As can be seen from these values, both reactions are slightly affected by vibrational and thermal contributions. However, the computed enthalpies for reactions 1 and 2, 71.8 and 19.1 kcal/mol, respectively, are in good agreement with the experimental estimates, 71.9 and 20.8 kcal/mol, respectively.[38,39] These findings support well the quality of our protocol. More important, if the entropic effects are included, the resulting free energies show the expected behavior: the dissociation free energy is lower than the free energy for the isomerization reactions, thus confirming the experimental postulate.

Starting from these results, only the Gibbs free energies will be discussed in the following.

3.2. Effects of the Substituents in Para Position. To investigate the effects of lateral groups on the two considered decomposition channels of nitrobenzene, five different substituents, namely nitro, methyl, amino, carboxylic acid, and hydroxyl (−NO_2, −CH_3, −NH_2, −COOH, −OH), have been considered. Their different electron donor or acceptor properties can be nicely summarized in terms of the Hammet constant (σ),[40] one of the most widely used means for the study and interpretation of reactions mechanisms and properties of organic compounds.[41,42] Its success was so large that a series of Hammett-like equations have been derived using different molecular descriptors.[43] A positive value of σ indicates that the substituent group is electron withdrawing in nature and the reactivity of the nitro-derivative is expected to be high; on the other hand a negative value implies the electron-donating nature of the substituent and the reactivity of the molecule is thus lower.

The experimental values for the para and meta positions, taken from ref 42 are collected in Table 2. We recall that the Hammett equation breaks down for ortho substituents, which exert significant "proximity" effects that may be polar as well as steric in origin, and therefore more difficultly represented by a very simple relationship such as the Hammett equation.

As expected, the nitro group is the most electron-withdrawing group (0.71), and the amino substituent is the most electron-donating group (−0.16). Thus, the σ-values suggest a higher reactivity in the first case than in the second. The donor/acceptor properties of the different lateral substituents are also reflected in the total charge beard by the nitro group. These charges, obtained by a NPA technique, are reported in Table 3 and they are very close to those obtained using the Mulliken definition[44] (not reported in the table). Nevertheless, their variations are in a narrow range with the charges being between −0.23 (−NO_2) and −0.30 (−NH_2) $|e^-|$.

The electronic structure is related to the geometrical rearrangements so that longer carbon−nitrogen distances are found for the nitrobenzenes substituted with the strongest electron attractor groups. The variation range (between 1.448 and 1.472
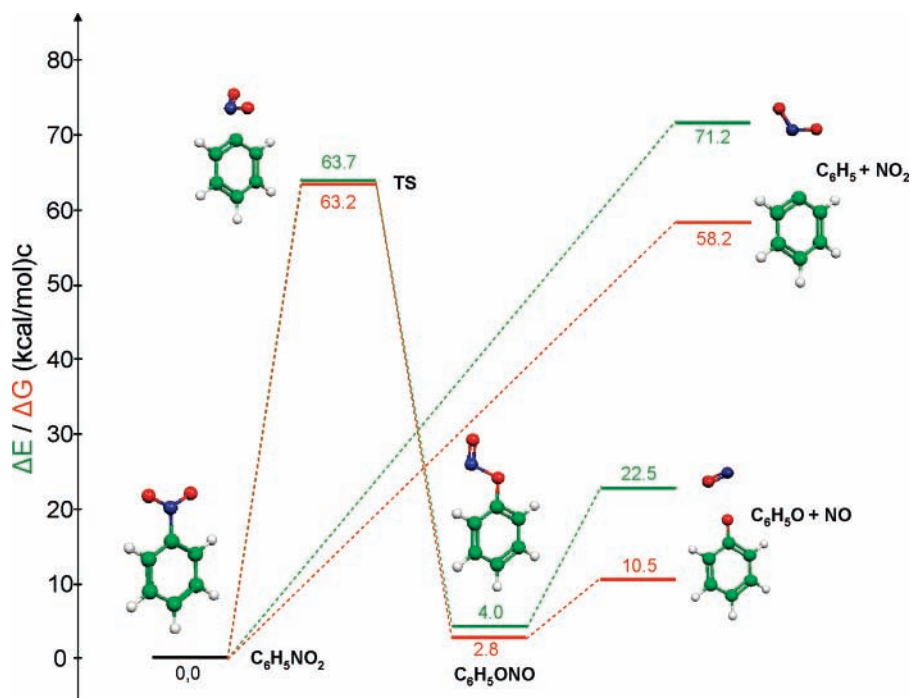
Figure 2. The relative energies (ΔE, green) and Gibbs free energies (ΔG, red) for the nitrobenzene decomposition pathways calculated at the PBE0/6-31+G(d,p) level.

TABLE 1: Relative Energies (ΔE), Enthalpies (ΔH), and Gibbs Free Energies (ΔG) in kcal/mol for the Dissociation Reactions to NO and NO$_2$ of Nitrobenzene at PBE0/6-31+G(d,p)

	ΔE		ΔH	ΔG
	PBE0	G2M[a]	PBE0	PBE0
$C_6H_5NO_2$	0.0	0.0	0.0	0.0
TS	63.7	61.1	63.7	63.2
C_6H_5ONO	4.0	1.1	4.0	2.8
C_6H_5O + NO	22.5	23.6	23.1	10.5
C_6H_5 + NO$_2$	71.2	74.1	71.8	58.2

[a] From ref 7, G2M(RCC,MP2)//B3LYP/6-311G(d,p) level.

TABLE 2: Experimental Hammett Constants from Reference 42

	σ_m	σ_p
−H	0.00	0.00
−NO$_2$	0.71	0.78
−CH$_3$	−0.07	−0.17
−NH$_2$	−0.16	−0.66
−COOH	0.37	0.45
−OH	0.12	−0.37

TABLE 3: Atomic Charge ($|e^-|$) of the NO$_2$ Group Computed from a Natural Population Analysis

	para	meta	ortho
−H	−0.26	−0.26	−0.26
−NO$_2$	−0.23	−0.23	−0.20
−CH$_3$	−0.26	−0.26	−0.26
−NH$_2$	−0.30	−0.26	−0.33
−COOH	−0.24	−0.24	−0.22
−OH	−0.28	−0.25	−0.25

Å) is relatively important in the para-substituted molecules, as can be seen from the data collected in Supporting Information, Table S1.

The Gibbs free energies for the two decomposition reactions are collected in Table 4 and summarized in Figure 3. From a general point of view, the dissociation channel is slightly lower in energy than the TS for the isomerization to phenylnitrite of

TABLE 4: Relative Gibbs Free Energies (kcal/mol) for the Dissociation Reactions to NO and NO$_2$ of Substituted Nitroaromatic Compounds (for Comparison Purpose Also the Nitrobenzene Energies Are Reported (column -H))

	−H	−NO$_2$	−CH$_3$	−NH$_2$	−COOH	−OH
			para			
$C_6H_5NO_2$	0.0	0.0	0.0	0.0	0.0	0.0
TS	63.2	60.7	64.3	66.9	61.4	65.9
C_6H_5ONO	2.8	0.4	3.9	6.6	1.4	5.1
$C_6H_4O(X)$ + NO	10.5	10.1	9.1	7.6	10.2	9.0
$C_6H_4(X)$ + NO$_2$	58.2	56.2	59.4	63.0	56.9	61.0
			meta			
$C_6H_5NO_2$	0.0	0.0	0.0	0.0	0.0	0.0
TS	63.2	62.9	63.5	63.4	63.4	63.0
C_6H_5ONO	2.8	1.3	3.2	3.5	2.4	2.7
$C_6H_4O(X)$ + NO	10.5	10.5	11.1	10.7	10.9	10.9
$C_6H_4(X)$ + NO$_2$	58.2	55.9	58.4	59.0	57.5	58.0
			ortho			
$C_6H_5NO_2$	0.0	0.0	0.0	0.0	0.0	0.0
TS	63.2	54.6	58.9	64.4	55.9	68.8
C_6H_5ONO	2.8	−3.4	0.3	6.3	−1.7	7.0
$C_6H_4O(X)$ + NO	10.5	5.7	6.0	4.0	6.8	11.8
$C_6H_4(X)$ + NO$_2$	58.2	47.8	55.1	63.0	50.1	62.1

reaction 2 with the difference being an average of 4 kcal/mol. Electron-withdrawing groups have a significant effect on the barrier from the 63 kcal/mol for the reference nitrobenzene to the 61 kcal/mol for the 1,4-dinitrobenzene or for the 4-nitrobenzoic acid. Larger barriers are found for the electron-donating groups with the amino substituent showing the larger value (67 kcal/mol). The same trend is found for the relative stability of the phenylnitrite: more electron donor−acceptor is the substituent, lower is the energy difference with respect to the nitrobenzene (see Table 4). In contrast, the dissociation of the O−N bond leading to the phenoxy radical (C_6H_5O), which is the last step of this reaction channel, requires around 10 kcal/mol, and the effect of the substituent is limited.

Larger substituent effects are found also on the direct breaking of the C−NO$_2$ bond (reaction 1): the corresponding Gibbs free energies range between 56 (NO$_2$) and 63 kcal/mol (NH$_2$). Once

Decomposition Reactions in Substituted Nitrobenzenes

J. Phys. Chem. A, Vol. 112, No. 17, 2008 **4057**
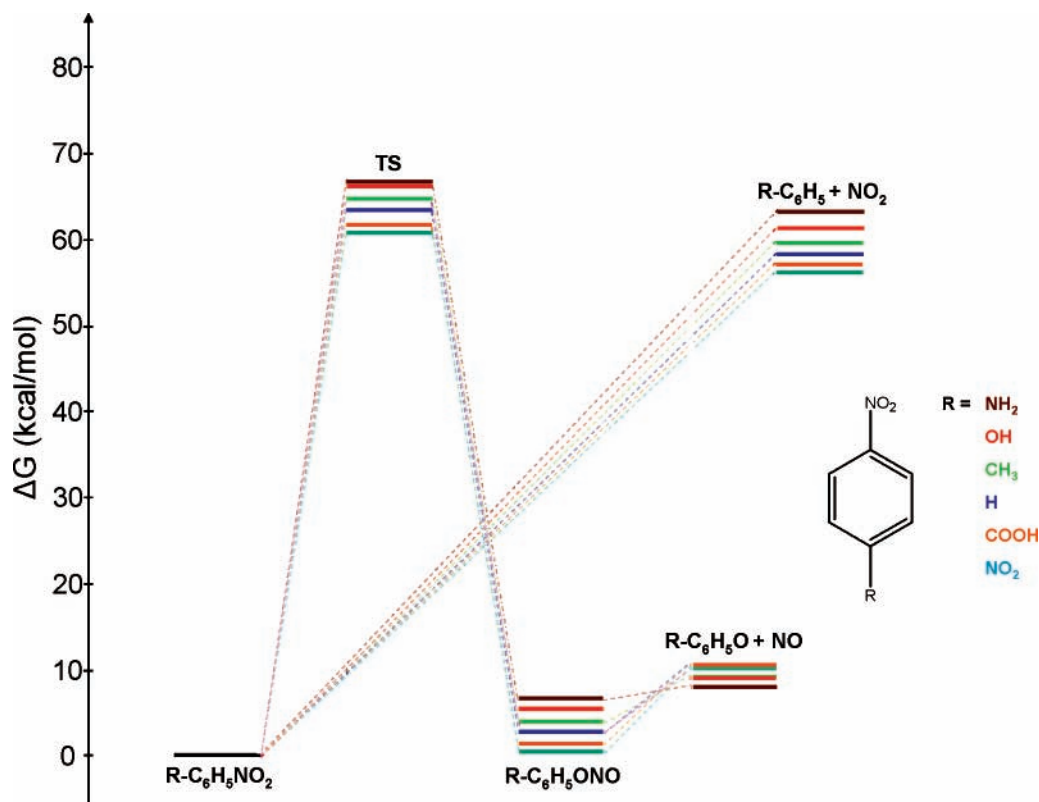
Figure 3. Relative Gibbs free energy diagram for dissociation reactions to NO and NO_2 of p-substituted nitrobenzenes calculated at the PBE0/6-31+G(d,p) level.
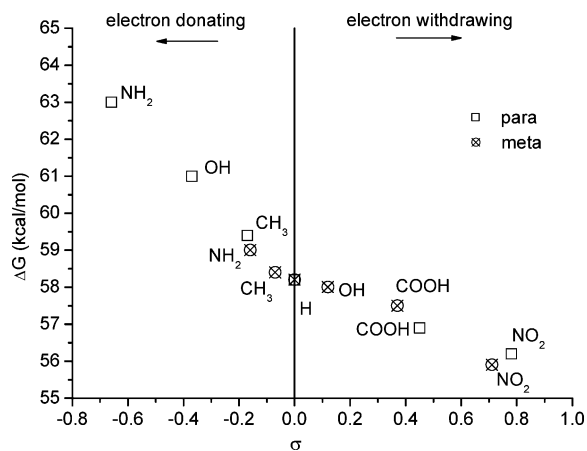
Figure 4. Computed Gibbs free energy variations as a function of the experimental Hammett constant for the dissociation of the $C-NO_2$ bond for meta- and para-substituted nitrobenzenes.

again, the energy is directly related to the electron attraction power of the lateral group. It is therefore interesting to note the linear relation ($R^2 = 0.94$) between the Gibbs free energies for the $C-NO_2$ bond dissociations and the Hammett parameters (Figure 4). A similar linear relation can be found for the σ with the ΔG for the relative stabilities of the different phenylnitrites. A breakdown of the Hammett relation is observed for the barrier heights of the isomerization. A similar failure of the predictive power of the Hammett equation has been already found for activation energies of conformational equilibria.[45]

A direct comparison of the ratio between the rate-controlling barriers for the isomerization and the cleavage energy of the $C-NO_2$ bond shows that it does not change for the different substituents. Electron-withdrawing substituents weaken the $C-N$ bond and stabilize the nitrite intermediate. At the same time, electron-donating substituents destabilize the $C-N$ bond cleav-

age product as much as the nitrite intermediate so that the mechanistic competition does not change significantly. In other words, the electron donor–acceptor characteristics of the substituent in para position to the NO_2 group do not strongly influence the balance of reaction 1 and 2. The competition between the two channels is an intrinsic property of the parent system (nitrobenzene) only slightly tuned by the para-substituent. These results are somewhat in contrast with the experimental data obtained, using other substituents, by mass spectrometry.[27]

3.3. Influence of Meta-Substituents. The same analysis was conducted for the meta-substituted nitrobenzenes. The optimized structures are reported in Supporting Information, Table S2, whereas NPA charges are collected in Table 3. In this case only a small effect of the substitution in meta position is observed for both geometrical and electronic parameters. In fact, the $C-NO_2$ distance does not depend upon the substituent (variations of less than 0.004 Å in Supporting Information, Table S2) and the charge of the nitro group is always around $-0.24 \ |e^-|$.

Minor variations are also found on the decomposition paths, as can be seen from the plot of Figure 5 and the data reported in Table 4. The TS energies for the isomerization are all about 63.0 kcal/mol. A larger dispersion is observed for the relative stability of the phenylnitrite product (ΔG between 1 and 3 kcal/mol). Concerning the final products (phenoxy radical and nitric oxide) they are about 10 kcal/mol less stable than the original nitrobenzene.

A larger deviation (3 kcal/mol) is also found between the Gibbs free energies for the $C-NO_2$ dissociations: they range between 56 (NO_2) and 59 (NH_2) kcal/mol, following the electronic properties of the substituent. In fact, there is a linear dependency ($R^2 = 0.96$) of such energies upon the Hammett parameters (Table 3), as can be seen from the plot of Figure 4. As for the para-substituents, the same holds for the energy of the phenylnitrite but not for the energies of the corresponding
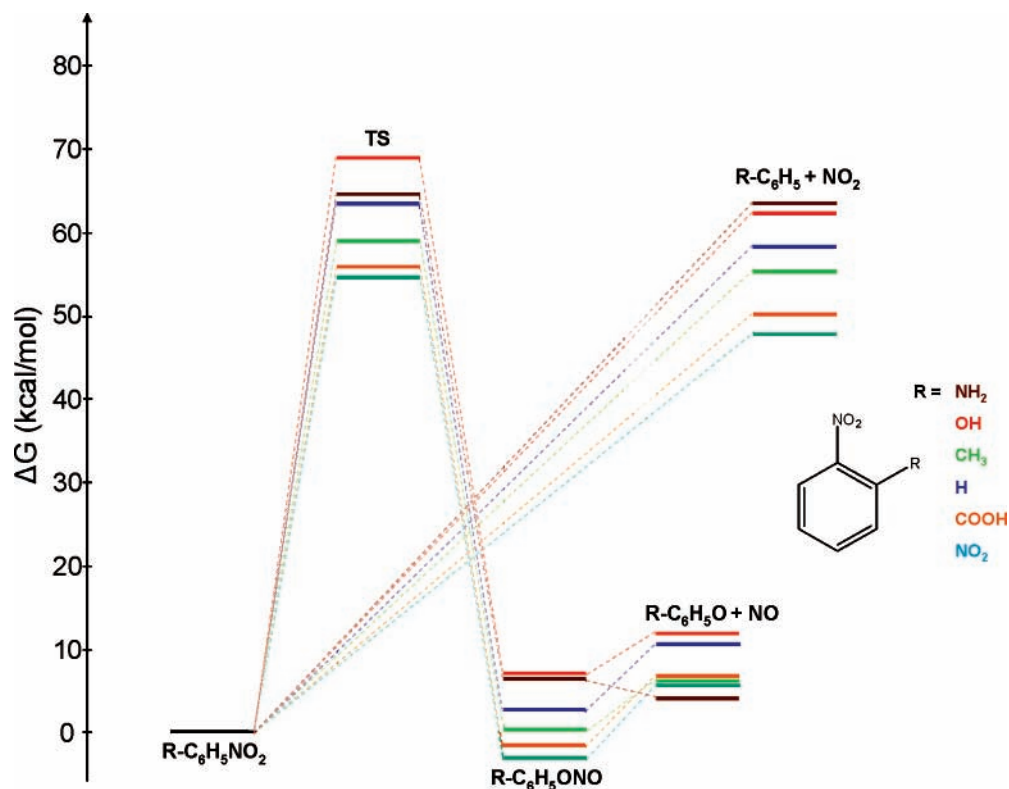
Figure 5. Relative Gibbs free energy diagram for dissociation reactions to NO and NO_2 of o-substituted nitrobenzenes calculated at the PBE0/6-31+G(d,p) level.

TSs. It is interesting also to note that the reactivity of the substituted nitrobenzenes is not affected by the positions of the two most electron-withdrawing groups (NO_2, COOH), while significant variations are found for the most electron-donating substituents (CH_3, NH_2). In the middle, the Hammett constant of the hydroxyl group changes sign from the para to the meta position. These observations can be explained by the resonance effect of the hydroxyl group on the aromatic molecules, which concern only the para (and ortho) position, not meta.

Finally, the energy difference between the TS and the C—NO_2 bond breaking, as an indicator of the competition between the two channels, slightly increases with respect to the meta-substituted nitrobenzene. Nevertheless, bond breaking is still the process lower in energy.

3.4. Influence of Ortho-Substituents. The electron donor–acceptor properties of ortho-substituents are more difficult to interpret because of the interaction between the nitro group and the close substituent. Geometric structures (in Supporting Information, Table S3) and NO_2 charges (Table 3) are influenced by the nature of the ortho-substituent but such effects cannot be straightforward classified as for the para and meta positions. For example, the C—N distance is smaller for —CH_3 than for —OH whereas it was the opposite in the para position. Still the most electron attractor groups (NO_2 and COOH) show the larger bond lengths and the smaller charges on the nitro group.

This observation is also in agreement with the decomposition channels. Some differences in Gibbs free energies appear in Figure 5 according to the substituents but the decomposition behavior is difficultly connected to the electron donor–acceptor abilities. In particular, for nitro, methyl, and carboxyl groups the energy barriers to phenylnitrite are lower than for the para- or meta-substituted systems, whereas it is higher for hydroxyl group. The amino substituent presents an intermediate behavior: the barrier for the ortho position is higher than for the meta one, but lower than for the para substitution. More interesting,

the ortho substitution leads to phenylnitrite derivatives that are more stable than the parent nitrobenzene for NO_2 and COOH, both showing the lowest barriers for the isomerization (−55 and −56 kcal/mol, respectively).

Even lower energies are found for the dissociation channel, thus showing the strong stabilizing effects of the ortho substituent on the resulting phenyl radical. This last reaction is always favored over the isomerization the differences in ΔG ranging between 4 (CH_3) and 7 kcal/mol (NO_2, OH). The only exception is the amino derivative for which a small difference (1 kcal/mol) is found between the isomerization TS and the decomposition energy.

Nevertheless, it must be indicated that other and more complex reaction channels have been postulated to be major for ortho-substituted nitroaromatic molecules, involving the direct interaction of NO_2 with the ortho substituent.[27] Such reaction channels have been calculated for the 2-nitrotoluene[8] and the 2,4,6-trinitrotoluene (TNT).[9]

4. Conclusion

A theoretical study on the influence of substituent nature and position on the unimolecular decomposition of nitroaromatic compounds has been carried out using density functional theory at the PBE0/6-31+G(d,p) level. In particular, two major decomposition channels of nitrobenzene and several derivatives were analyzed, corresponding to direct carbon nitrogen dissociation (C_6H_5 + NO_2) and a two step mechanism leading to the formation of phenoxyl nitro radicals (C_6H_5O + NO). The Gibbs free energies were computed for 15 nitrobenzene derivatives characterized by different substituents (nitro, methyl, amino, carboxylic acid, and hydroxyl) in the ortho, meta, and para positions to the nitro group. In meta position, no significant changes appeared in the reaction energy profile, whereas ortho and para derivatives show significant deviations for the decom-

Decomposition Reactions in Substituted Nitrobenzenes

J. Phys. Chem. A, Vol. 112, No. 17, 2008 **4059**

position mechanisms, thus bringing to light the mesomeric effect of the nitro group. In the case of para and meta substitution, the carbon−nitro bond dissociation energy has been directly related to the Hammett constant as an indicator of the electron donor−acceptor effect of substituents.

These results confirm the experimental assumption that the direct breaking of the C−N bond is responsible for the heat generated at the explosion. However, isomerization to phenylnitrite could be not too far in energy for electron donor groups (as NH_2) to be considered as competitive, especially at high temperature.

Supporting Information Available: Tables of main structural parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Etchells, J. C. *Org. Process Res. Dev.* **1997**, *1*, 435.
(2) Gustin, J. L. *Org. Process Res. Dev.* **1998**, *2*, 27.
(3) Shanley, E. S.; Melhem, G. A. *J. Loss Prev. Process Ind.* **1995**, *5*, 261.
(4) Melhem, G. A.; Shanley, E. S. *Process Safety Prog.* **1996**, *15*, 168.
(5) Lewis, A.; Kazantzis, N.; Fishtik, I.; Wilcox, J. *J. Hazard. Mater.* **2007**, *142*, 592.
(6) Lothrop, W. C.; Handrick, G. R. *Chem. Rev.* **1949**, *44*, 419.
(7) Xu, S.; Lin, M. C. *J. Phys. Chem. B* **2005**, *109*, 8367.
(8) Chen, S. C.; Xu, S. C.; Diau, E.; Lin, M. C. *J. Phys. Chem. A* **2006**, *110*, 10130.
(9) Cohen, R.; Zeiri, Y.; Wurzberg, E.; Kosloff, R. *J. Phys. Chem. A* **2007**, *111*, 11074.
(10) Gindulyte, A.; Massa, L.; Huang, L.; Karle, J. *J. Phys. Chem. A* **1999**, *103*, 11040.
(11) Gindulyte, A.; Massa, L.; Huang, L.; Karle, J. *J. Phys. Chem. A* **1999**, *103*, 11045.
(12) Liu, M. H.; Chen, C.; Hong, Y. S. *Int. J. Quantum Chem.* **2005**, *102*, 398.
(13) Nefati, H.; Cense, J. M.; Legendre, J. J. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 804.
(14) Katritzky, A. R.; Petrukhin, R.; Jain, R.; Karelson, M. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 1521.
(15) Keshavarz, M. H. *J. Hazard. Mater.* **2007**, *142*, 54.
(16) Shanley, E. S; Melhem, G. A *Process Safety Prog.* **1995**, *14*, 29.
(17) Grewer, T. *Thermochim. Acta* **1991**, *187*, 133.
(18) Kersen, R. J. A.; Boers, M. N.; Stork, M. M.; Visser, C. *J. Loss. Prev. Process Ind.* **2005**, *18*, 145.
(19) Medard, L. *Les explosifs occasionnels-Tomes 1 & 2*, TEC & DOC: Cachan, France, 1987.
(20) Gonzales, A. C.; Larson, C. W.; McMillen, D. F.; Golden, D. M. *J. Phys. Chem.* **1985**, *89*, 4809.
(21) Tsang, W.; Robaugh, D.; Mallard, W. G. *J. Phys. Chem.* **1986**, *90*, 5968.
(22) Galloway, D. B.; Bartz, J. A.; Huey, L. G.; Crim, F. F. *J. Chem. Phys.* **1993**, *98*, 2107.
(23) Galloway, D. B.; Glenewinckel-Meyer, T.; Bartz, J. A.; Huey, L. G.; Crim, F. F. *J. Chem. Phys.* **1994**, *100*, 1946.
(24) Kosmidis, C.; Ledingham, K. W. D.; Kilic, H. S.; McCanny, T.; Singhal, R. P.; Langley, A. J.; Shaikh, W. *J. Phys. Chem. A* **1997**, *101*, 2264.
(25) Li, Y. M.; Sun, J. L.; Yin, H. M.; Han, K. L.; He, G. Z. *J. Chem. Phys.* **2003**, *118*, 6244.
(26) McCarthy, E.; O' Brien, K. *J. Org. Chem.* **1980**, *45*, 2086.
(27) Brill, T. B.; James, K. J.; Chawla, R.; Nicol, G.; Shukla, A.; Futrell, J. H. *J. Phys. Org. Chem.* **1999**, *12*, 819.
(28) Brill, T. B.; James, K. J. *Chem. Rev.* **1993**, *93*, 2667.
(29) Saraf, S. R.; Rogers, W. J.; Mannan, M. S. *Ind. Eng. Chem. Res.* **2003**, *42*, 1341.
(30) Theerlynck, E.; Mathieu, D.; Simonetti, P. *Thermochim. Acta* **2005**, *426*, 123.
(31) Shao, J.; Cheng, X.; Xiangdong, Y. *Struct. Chem.* **2006**, *17*, 547.
(32) Rice, B. M.; Sahu, S.; Owens, F. J. *J. Mol. Struct. (Theochem)* **2002**, *583*, 69.
(33) Politzer, P.; Seminario, J. M.; Bolduc, P. R. *Chem. Phys. Lett.* **1989**, *158*, 463.
(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Pittsburgh, PA, 2003.
(35) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.
(36) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736.
(37) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(38) Luo, J. X. *Handbook of bond dissociation energies in organic compounds*; CRC Press: Boca Raton, FL, 2003.
(39) Berho, F.; Caralp, F.; Rayez, M. T.; Lesclaux, R.; Ratajczak, E. *J. Phys. Chem. A* **1998**, *102*, 1.
(40) Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 96.
(41) Jacquemin, D.; Champagne, B.; André, J. M. *Synth. Met.* **1996**, *80*, 205.
(42) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.
(43) Pérez, P.; Simon-Manso, Y.; Aizman, A.; Fuentalba, P.; Contreras, R. *J. Am. Chem. Soc.* **2000**, *122*, 4756.
(44) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.
(45) Palat, K.; Böhm, S.; Braunerova, G.; Waisser, K.; Exner, O. *New. J. Chem.* **2002**, *26*, 861.