Theoretical study on pyrolysis and sensitivity of energetic compounds. Part 4. Nitro derivatives of phenols

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ABSTRACT: The UHF–SCF–AM1 MO method was applied to the study of two kinds of pyrolysis reactions of six nitro derivatives of phenols (homolysis reaction by rupture of the C—NO_2 bond into radicals and isomerization reaction involving phenolic hydrogen transferring to oxygen on the NO_2 group). The molecular geometries of reactants, transition states and products were fully optimized. The potential energy curves and activation energies were first obtained. The results show that this category of compounds is more easily initiated via isomerization reactions than by homolysis reactions. The parallel relationship among the Wiberg bond order of the pyrolysis-initiation H—O bond in the molecule of a reactant, the activation energy of the isomerization reaction breaking the H—O bond and impact sensitivity of the reactant gives 'the principle of the smallest bond order' (PSBO) powerful support. The sensitizing effect of a phenol group was elucidated based on calculation results. The different influences of OH and NO_2 groups on the heat of formation of a molecule are discussed. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: nitro derivatives of phenols; pyrolysis initiation reactions; impact sensitivity; UHF–SCF–AM1 MO method; activation energy.

INTRODUCTION

The sensitivity of energetic compounds to stimuli such as impact and shock has received considerable attention from chemists for several decades. A deep investigation into the factors that determine the sensitivity is essential for the design and development of new energetic systems with high performance.

The nitro derivatives of phenols are an important category of energetic compounds. 2,4,6-Trinitroresorcinol (styphnic acid) and 2,4,6-trinitrophenol (picric acid) are well known explosives. Picric acid has been found to be sensitive, and the same is true for the di- and trihydroxy systems.

It is widely accepted that the phenol group is family active, which influences the sensitivity of an explosive. Politzer and Seminario[1] reported that hydroxyl derivatives of nitroaromatics possess different sensitivity to amino derivatives. Hydroxyl substituents sensitize nitroaromatic molecules towards shock and impact, despite having resonance capabilities.

With regard to the impact sensitivity of nitro derivatives of phenols, we successfully applied 'the principle of the smallest bond order' (PSBO) to identify their relative magnitudes of impact sensitivity, and obtained bond orders of the pyrolysis-initiation bonds (H—O bond in a phenolic group) in their molecules. The principle pointed out that for a series of compounds with similar molecular structures, the larger the value of the bond order of the pyrolysis-initiation bond, the lower becomes the impact sensitivity of the compound, and the smallest bond order of the pyrolysis-initiation bond corresponds to the greatest sensitivity of the compound.[2–5]

Modern theoretical studies of pyrolysis mechanisms of most nitroaromatics show that their pyrolysis usually starts with the scission of the weakest bond (e.g. C—NO_2 bond) in a molecule.[2,6,7] However, for this category of compounds, most experimental results support the viewpoint that molecules are initiated via an isomerization reaction, taking place via phenolic hydrogen transferring to oxygen on the *ortho*-NO_2 group.[8–10] Our early MO calculations[2] also supported this mechanism. Politzer and Seminario[1] obtained the optimized structure of the nitronic acid tautomer of *o*-nitrophenol at the SCF 3–21G level. So far no theoretical calculation of pyrolysis-initiation reactions of nitro derivative of phenols has been reported. Hence the question arises of whether the calculation for the reactions also supports this pyrolysis-initiation mechanism with an isomerization reaction or a mechanism in which pyrolysis of molecules is initiated

by the rupture of the C—NO$_2$ bond in the same way as in other nitroaromatics such as nitro derivatives of benzene and aminobenzenes.[2,6,7]

Early MO calculations[11–14] on the homolysis reactions of nitro compounds and nitroamines showed that the restricted Hartree–Fock (RHF) method only provided potential energy curves on which molecular energies increased with the initiation bond length. It is obvious that the RHF method cannot describe homolysis processes and the use of the unrestricted Hartree–Fock (UHF) MO method is a minimal requirement. It has been successfully applied for studying the mechanisms of pyrolysis-initiation reactions of five model energetic molecules,[15] nitro derivatives of benzene and aminobenzenes.[6,7] For isomerization reactions, UHF and RHF MO methods are both feasible. In this work, in order to compare the results for two kinds of pyrolysis reactions, all the calculations were carried out with the UHF MO method.

This is the fourth paper in the series on the theoretical study on pyrolysis mechanisms and impact sensitivities of energetic compounds. The UHF–SCF–AM1 method was applied to study two kinds of pyrolysis-initiation reactions of six nitro derivatives of phenols, i.e. 2,4-dinitrophenol (**1**), 4,6-dinitroresorcinol (**2**), 2,4-dinitroresorcinol (**3**), 2,4,6-trinitrophenol (**4**), 2,4,6-trinitroresorcinol (**5**) and 2,4,6-trinitro-1,3,5-trihydroxybenzene (**6**). The molecular geometries of the reactants, transition states and products were fully optimized. The potential energy curves and activation energies of two kinds of reactions for each of the above molecules (total 12 reactions) were first obtained. By comparing the activation energies of two kinds of reactions, it was concluded that nitro derivatives of phenols are more easily initiated via isomerization reactions. Molecular geometric changes in these reactions were explored. Further, the results showed that there is a parallel relationship among the Wiberg bond order of the pyrolysis-initiation H—O bond in a reactant molecule, the activation energy of the isomerization reaction breaking the H—O bond and the impact sensitivity of the reactant, which gives PSBO powerful support. The sensitizing effect of the phenol group was elucidated based on calculation results. Also, the different influences of OH and NO$_2$ groups on the heat of formation of a molecule are discussed.

CALCULATION METHOD AND RESULTS

The UHF–SCF–AM1[16] MO method included in the Mopac 5.0 program package[17] was applied to study two kinds of pyrolysis mechanisms of six nitro derivatives of phenols, shown as equations (1) and (2), respectively, with 2,4-dinitrophenol as an example. The initial geometries of reactants were based on the Pople and Beveridge's standard data[18] and were subsequently optimized with an energy gradient method. The α and β

electronic orbitals and energies were obtained from UHF MO calculations.
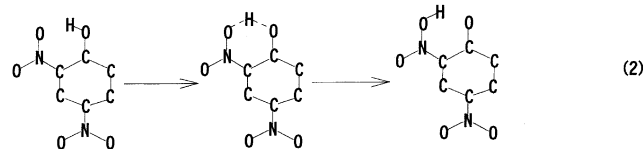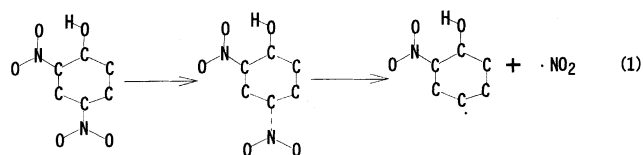
In homolysis reactions shown as equation (1), the distance between the C atom in the benzene ring and the N atom in the NO$_2$ group (corresponding to the weakest C—NO$_2$ bond with the smallest value of Wiberg bond order[19] among all the C—NO$_2$ bonds in a reactant molecule) was chosen as the reaction coordinate. It corresponds to the bond C(2)—NO$_2$ in 2,4-dinitroresorcinol (**3**) and 2,4,6-trinitro-1,3,5-trihydroxylbenzene (**6**), the bond C(4)—NO$_2$ in 2,4-dinitrophenol (**1**) and 4,6-dinitroresorcinol (**2**) and the bond C(6)—NO$_2$ in 2,4,6-trinitrophenol (**4**) and 2,4,6-trinitroresorcinol (**5**), based on the Wiberg bond order in each reactant molecule.

For isomerization reactions shown as equation (2), the distance between the O and H atoms in the phenolic OH group was adopted as the reaction coordinate. It corresponds to the bond H—O(7) in each reactant molecule, which is the weakest H—O bond with the smallest value of the Wiberg bond order among all the H—O bonds in a reactant molecule (see Fig. 1).

Calculations were carried out for the above two kinds of pyrolysis reactions by changing the reaction coordinate in steps of 0.1 Å from 1.4 to 3.5 Å for a homolysis reaction and from 1.0 to 2.0 Å for an isomerization reaction. The molecular geometries were optimized at different values of the reaction coordinate. In total calculations were made for 12 reactions. The potential energy curve for each reaction was obtained based on the result of heats of formation at different single points on the reaction coordinate. The transition state was obtained by optimizing the structure corresponding to the highest point of the potential energy curve with the NLLSQ method,[20] and was confirmed with only one imaginary vibration. All the calculations were performed on an HP-9000-842 computer.

Figure 1 shows the optimized geometries of six nitro derivatives of phenols, the numbering of some atoms and the results for the Wiberg bond order of some bonds in the molecules. Figure 2 depicts the optimized geometries of the reactant, transition state and product in the isomerization reaction of 2,4-dinitrophenol. Also shown are the results for net charges on some atoms in the optimized species. Tables 1 and 2 list the heats of

Figure 1. Optimized geometries (bond lengths in ångstroms, bond angles in degrees) of six nitro derivatives of phenols, numbering of some atoms and the results for Wiberg bond order (in parentheses) of some bonds in the optimized species
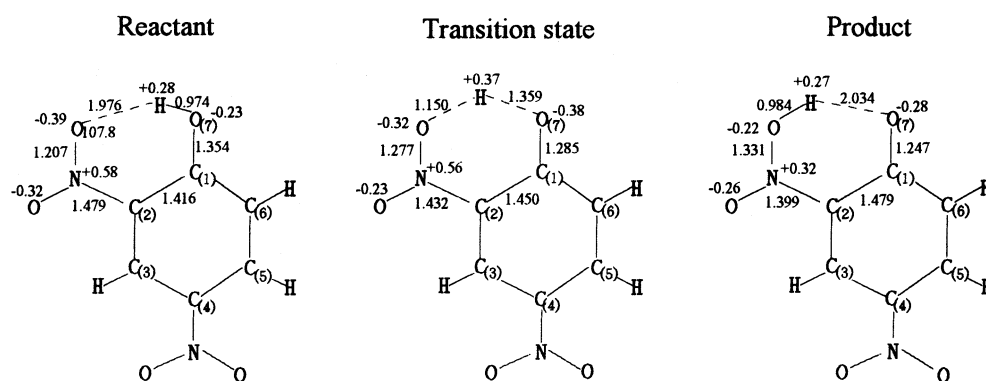
Figure 2. Optimized geometries of reactant, transition state and product in the isomerization reaction of 2,4-dinitrophenol (bond lengths in ångstroms, bond angles in degrees) and the net charges on some atoms in the optimized species

formation of optimized species and the activation energies of six homolysis reactions and six isomerization reactions, respectively. Figure 3 (a) and (b) illustrate the potential energy curves for six homolysis reactions and six isomerization reactions, respectively. Table 3 contains the impact sensitivities of six compounds, the activation energies for the two kinds of reactions and the results for the Wiberg bond order in the reactant molecules.

DISCUSSION

Molecular geometries, electronic structures and heats of formation of reactants

The optimized geometries and electronic structure parameters for the molecules of the six nitro derivatives of phenols are illustrated in Fig. 1. The calculation results show that the N atom in the NO_2 group in each reactant molecule exists in an sp^2 hybrid state, with a bond angle $\angle ONO$ of about $120°$ and an N—O bond length of about 1.2 Å.

Hydrogen bonds exist in all the six reactant molecules (see Fig. 1). The distance between the phenolic H and the O atom in the *ortho*-NO_2 group is about 1.90–1.98 Å in each reactant molecule. The optimized geometries of all six molecules are planar, showing that all the NO_2 and OH groups are nearly in the benzene ring plane. This results from good conjugation and hydrogen bond effects.

From the UHF–SCF–AM1 calculations, the Wiberg bond order of the weakest C—NO_2 bond in each reactant molecule was obtained. It is 0.859, 0.879, 0.885, 0.852, 0.858 and 0.886 in the molecules of compounds **1–6,** respectively, corresponding to the C(4)—NO_2, C(4)—NO_2, C(2)—NO_2, C(6)—NO_2, C(6)—NO_2 and C(2)—NO_2 bonds, respectively (see Fig. 1). Their optimized bond lengths are 1.486, 1.477, 1.476, 1.491, 1.488 and 1.477 Å , respectively.

Isomerization reaction via a phenolic hydrogen transferring to oxygen in the NO_2 group involves the rupture of the H—O bond in the phenolic hydroxyl group. The Wiberg bond orders of the weakest H—O bond in the phenolic hydroxyl groups in each reactant molecule were obtained as 0.886, 0.885, 0.878, 0.877, 0.869 and 0.866 for **1–6,** respectively, each corresponding to the H—O(7) bond (see Fig. 1). The optimized bond lengths in the molecules of **1–6** are 0.974, 0.974, 0.975, 0.977, 0.978 and 0.978 Å , respectively.

Also obtained were the net charges on atoms in the optimized species. Here we only illustrate the results for 2,4-dinitrophenol in Fig. 2 for the sake of brevity. In each

Table 1. Heats of formation of optimized species and activation energies (E_a^h) of six homolysis reactions (kJ mol^{-1})

Reaction[a]	Heat of formation			Activation energy[b] (E_a^h)
	Reactant	Transition state	Product	
I	−55.522	98.826	69.567	136.859
II	−247.881	−84.646	−116.658	146.289
III	−235.890	−76.287	−109.039	143.369
IV	4.916	154.611	118.742	133.691
V	−179.531	−31.288	−64.530	132.495
VI	−362.744	−205.208	221.564	142.812

[a] I, II, … VI represent the numbering of the homolysis reactions of 2,4-dinitrophenol (**1**), 4,6-dinitroresorcinol (**2**), 2,4-dinitroresorcinol (**3**), 2,4,6-trinitrophenol (**4**), 2,4,6-trinitroresorcinol (**5**) and 2,4,6-trinitro-1,3,5-trihydroxylbenzene (**6**), respectively.
[b] The activation energy has been modified with the zero point energy, i.e. $E_a^h = (E_{TS} + T_{TS}^0) - (E_R + E_R^0)$, where E_R^0 and E_{TS}^0 are zero point energies of the reactant and transition state of a homolysis reaction and E_R and E_{TS} are their heats of formation, respectively.

Table 2. Heats of formation of optimized species and activation energies (E_a^i) of six isomerization reactions (kJ mol^{-1}).

Reaction[a]	Heat of formation			Activation energy[b] (E_a^h)
	Reactant	Transition state	Product	
I	−55.522	61.597	26.004	94.889
II	−247.881	−128.231	−152.017	97.613
III	−235.890	−133.143	−159.783	81.350
IV	4.916	112.462	83.291	85.475
V	−179.531	−86.069	−113.876	72.094
VI	−362.744	−274.583	−297.817	67.354

[a] I, II, … VI represent the numbering of the homolysis reactions of 2,4-dinitrophenol (**1**), 4,6-dinitroresorcinol (**2**), 2,4-dinitroresorcinol (**3**), 2,4,6-trinitrophenol (**4**), 2,4,6-trinitroresorcinol (**5**) and 2,4,6-trinitro-1,3,5-trihydroxylbenzene (**6**), respectively.
[b] The activation energy has been modified with the zero point energy, i.e. $E_a^h = (E_{TS} + T_{TS}^0) - (E_R + E_R^0)$, where E_R^0 and E_{TS}^0 are zero point energies of the reactant and transition state of a homolysis reaction and E_R and E_{TS} are their heats of formation, respectively.

reactant molecule, the net charges on the OH groups are all positive, whereas those on the NO$_2$ groups are negative, which indicates that NO$_2$ is an electron-attracting group and OH is an electron donor.

On the basis of the results for the heats of formation of the reactant molecules in Tables 1 and 2, it is seen that the heat of formation of 2,4,6-trinitro-1,3,5-trihydroxylbenzene (**6**) is much lower than the others, whereas those of **1** and **4** are fairly high. It seems that the more OH groups there are in a molecule, the lower becomes the heat of formation. On the other hand, the difference among the heats of formation of **5, 3** and **2,** which all contain two OH groups, shows that the NO$_2$ group has a contrary effect on the heat of formation of a molecule. The more

NO$_2$ groups there are in a molecule, the higher becomes the heat of formation. Similarity is also observed between compounds **1** and **4**. This meaningful regularity also exists in other series compounds. We shall discuss this topic in detail later.

Pyrolysis-initiation mechanism

Two kinds of pyrolysis reactions for each compound were studied.

For a homolysis reaction shown as equation (1), with increase in the distance between the C atom on the benzene ring and the N atom in the NO$_2$ group
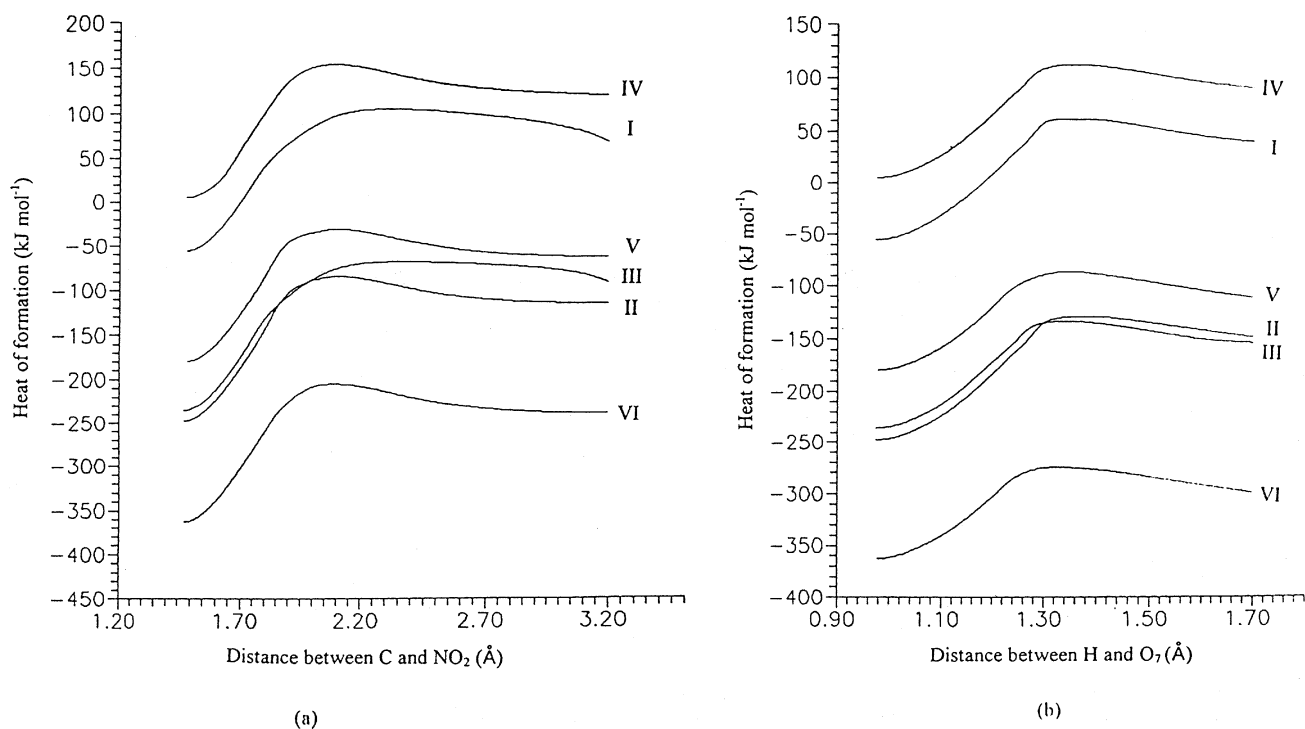
Figure 3. Potential energy curves for (a) homolysis and (b) isomerization reactions of six nitro derivatives of phenols. I–VI represent reaction of compounds **1–6,** respectively

Table 3. Impact sensitivity ($h_{50\%}$) of six nitro derivatives of phenols (**1–6**), their activation energies in two kinds of reactions (E_a^h and E_a^i) and the results for the Wiberg bond order in the reactant molecules (B_{C-NO_2} and B_{H-O}).

Parameter	**1**	**2**	**3**	**4**	**5**	**6**
$h_{50\%}$ (m)[a]		>3.2	2.96	0.87	0.43	0.27
E_a^h (kJ mol^{-1})[b]	136.859	146.289	143.369	133.691	132.495	142.812
E_a^i (kJ mol^{-1})	94.889	97.613	81.350	85.475	72.094	67.354
B_{C-NO_2}[c]	0.859	0.879	0.885	0.852	0.858	0.886
B_{H-O}	0.886	0.885	0.878	0.877	0.869	0.866

[a] The data represent the height from which a given weight (2.5 kg) must be dropped on the compound to produce detonation. Thus, the smaller the value given, the more sensitive the compound is towards impact impulse. The date are taken from Ref. 2.
b E_a^h and E_a^i correspond to the activation energies of homolysis and isomerization reactions, respectively.
c B_{C-NO_2} and B_{H-O} are the results for the Wiberg bond order of the weakest C—NO$_2$ and H—O bonds in a reactant molecule, respectively.

(corresponding to the weakest C—NO$_2$ bond), the net charge on each atom varies with the progress of the reaction. The net charges on the NO$_2$ groups in each reactant are negative, showing that the NO$_2$ group is an electron-attracting group. The net charge on the disengaged NO$_2$ group in each product of the homolysis reaction is zero, which verifies that the process is a radical dissociation. Calculations performed by changing the reaction coordinate (the distance between C and N atoms) show that the molecular energy first rises and then decreases slowly. Figure 3(a) illustrates the potential energy curves for six homolysis reactions. At a distance between the C and N atoms of about 2.1 Å, the transition state was formed. The heats of formation of reactants, transition states and products are listed in Table 1. The molecular energies of the products are higher than those of the reactants, which is consistent with the experimental fact that the process breaking a bond is endothermic. The activation energies (E_a^h) for the homolysis reactions for **1–6** are 136.859, 146.289, 143.369, 133.691, 132.495 and 142.812 kJ mol^{-1}, respectively.

For an isomerization reaction shown as equation (2), with increase in the distance between O and H in the phenolic hydroxyl group, it is found that phenolic hydrogen moves towards the N atom in the NO$_2$ group, forming a transition complex with a six-membered ring in which the distances between the phenolic H and the O in the *ortho*-NO$_2$ group are about 1.14–1.16 Å, and those between the phenolic H and O(7) are about 1.3–1.4 Å. The heats of formation of reactants, transition states and products are listed in Table 2. Figure 3(b) depicts the potential energy curves for the isomerization reactions of the six compounds, also showing that the molecular energies first rise and then decrease slowly via the reaction coordinate (the distance between H and O atoms in a phenolic hydroxyl group), and this process is also endothermic. The activation energies (E_a^i) of the isomerization reactions for **1–6** are 94.889, 97.613, 81.350, 85.475, 72.094 and 67.354 kJ mol^{-1}, respectively.

Table 3 shows that the activation energies of homolysis reactions are higher than those of isomerization

reactions by at least 40 kJ mol^{-1}, which means that molecules of the compounds under study are more likely initiated via an isomerization reaction taking place via the phenolic hydrogen transferring to the *ortho*-NO$_2$ group.

The six nitro derivatives of phenols studied possess a common point of structure that in each molecule there exists at least one NO$_2$ group *ortho* to a phenol group, which makes it possible for the phenolic H to transfer to the nitro O atom. It is well known that the special structure of *o*-nitrophenol accounts for certain properties by which it differs from the *m*- and *p*-isomers. So how the pyrolysis-initiation reactions of other nitro derivatives of phenols in which there is no NO$_2$ group *ortho* to a phenol group take place is still an unanswered question. This aspect will be studied in detail in future work.

Geometric and electronic structural variation in isomerization reactions

In isomerization reactions, the molecules of the compounds studied remain almost planar in the process of transfer of the phenolic hydrogen to the *ortho*-NO$_2$ group. The transition state contains a planar six-membered ring. As an example, the optimized geometries of the reactant, transition state and product in the isomerization reaction of 2,4-dinitrophenol and the net charges on some atoms in optimized species are illustrated in Fig. 2.

With increase in the reaction coordinate [the distance corresponding to the length of the H—O(7) bond], the distance between the phenolic H and the O in the *ortho*-NO$_2$ group decreases from 1.98 Å (reactant, R) to 1.15 Å (transition state, TS) to 0.98 Å (product, P), showing the phenolic H transferring towards the O atom in the NO$_2$ group. In product, this phenolic H bonds to the O atom in the NO$_2$ group with an ordinary H—O bond length, and a hydrogen bond exists between the phenolic O and itself with a length of about 2.0 Å. In the process of transfer of the phenolic H to the O atom in the *ortho*-NO$_2$ group, the C—OH bond length decreases from 1.35 Å (R) to 1.29 Å (TS) to 1.25 Å (P), displaying a double bond in the

product. In this process, the C(2)—NO_2 bond length also decreases from 1.48 Å (R) to 1.43 Å (TS) to 1.40 Å (P), while the O—N bond length in the *ortho*-NO_2 group increase from 1.21 Å (R) to 1.28 Å (TS) to 1.33 Å (P), showing a single bond in product due to the transfer of the phenolic H to this O atom, thus weakening this O—N bond.

Also observed are the large changes in the net charges on the phenolic O atom and the O atom in the *ortho*-NO_2 group. The former changes from −0.23 (R) to −0.38 (TS) to −0.28 (P), and the latter increases from −0.39 (R) to −0.32 (TS) to −0.22 (P), due to the binding of phenolic H with itself.

Wiberg bond order, activation energy and impact sensitivity

Table 3 shows the order of the experimental impact sensitivity to be **2** < **3** < **4** < **5** < **6**. The calculated activation energies of their isomerization reactions are 97.613, 81.350, 85.475, 72.094 and 67.354 kJ mol^{-1}, respectively, i.e. a similar order to the impact sensitivities except for **3**. The results for the Wiberg bond order of the pyrolysis-initiation H—O bonds in the isomerization reactions of **2–6** are 0.885, 0.878, 0.877, 0.869, 0.866, respectively. This order is identical with that of the impact sensitivities. However, for homolysis reactions, the activation energies and the results for the Wiberg bond order of the weakest C—NO_2 bonds in the reactant molecules (see Table 3) are in different orders both from each other and also from that of the impact sensitivities. This result also supports the contention that this category of compounds is probably not initiated via homolysis reactions. The meaningful regularity for the parallel relationship among the results for the Wiberg bond order of the pyrolysis-initiation H—O bonds, the activation energies of the isomerization reactions breaking the H—O bonds and the impact sensitivity of this category of compounds means that we only need to perform calculations for the reactant molecules to obtain the Wiberg bond order of the true pyrolysis-initiation bond, and then we can access its relative impact sensitivity. This result again gives the PSBO[2,3,4,5] powerful support.

In the previous work, UHF–SCF–AM1 calculations were also performed for the pyrolysis-initiation reactions of nitro derivatives of benzene and aminobenzenes.[6,7] The results showed that the activation energies for the initiation reactions of *s*-trinitrobenzene and 2,4,6-trinitroaminobenzene are 124.23 and 130.35 kJ mol^{-1}, respectively. In this study, the activation energy for the isomerization reaction of 2,4,6-trinitrophenol is 85.48 kJ mol^{-1}. Differences among the activation energies of the initiation reactions of these three compounds show that the phenol group possesses a sensitizing effect on nitroaromatics, whereas the amino group has a contrasting influence. The calculated results of activation energies in this work show that the more OH groups there are in a reactant molecule, the lower becomes the activation energy of its isomerization reaction and the more sensitive the compound is towards impact and shock impulse.

CONCLUSIONS

On the basis of UHF–AM1 MO calculations for two kinds of pyrolysis reactions of six nitro derivatives of phenols, it can be concluded that this category of compounds is more easily initiated via isomerization reactions via the phenolic hydrogen transferring to the O atom an the *ortho*-NO_2 group. The optimized geometries of the transition states exhibit a planar six-membered ring at about 1.3–1.4 Å on the reaction coordinate (the distance between the H and O atoms in the phenolic hydroxyl group). The activation energies of isomerization reactions of **1–6** are 94.889, 97.613, 81.350, 85.475, 72.094 and 67.354 kJ mol^{-1}, respectively. The parallel relationship among the Wiberg bond order of the pyrolysis-initiation H—O bond in the reactant molecules, the activation energies of isomerization reactions breaking the H—O bond and the impact sensitivity of the compounds gives the PSBO powerful support.

REFERENCES

1. P. Politzer and J. M. Seminario. *Chem. Phys. Lett.* **158,** 463 (1989).
2. H.-M. Xiao. *Molecular Orbital Theory of Nitro Compounds.* National Defense Industry Press, Beijing (1993).
3. H.-M. Xiao, Z.-Y Wang and J.-M. Yao. *Acta Chim. Sin.* **43,** 14 (1985).
4. H.-M. Xiao and Y.-F. Li. *Sci. China, Ser. B***38,** 538 (1995).
5. H.-M. Xiao, Y.-F. Li and P.-L. Feng. in *Proceedings of the International Symposium on Pyrotechnics and Explosives,* Beijing, October 1987, p. 434.
6. J.-F. Fan and H.-M. Xiao. *J. Mol. Struct. (THEOCHEM)* **365,** 225 (1996).
7. H.-M. Xiao, Z.-M. Gu and J.-F. Fan. *Chem. Phys.* in press.
8. V. G. Matveen, V. V. Dubikhin and G. M. Nazin. *Izv. Akad. Nauk SSSR, Ser. Khim.* **2,** 474 (1978).
9. M. Coellen and C. Ruechardt. *Chem. Eur. J.* **1,** 564 (1995).
10. T. Urbánski. *Chemistry and Technology of Explosives,* Vol. 1. Pergamon Press, Oxford (1964).
11. J. J. Kaufman, P. C. Hariharan, C. Chabalowshi and M. Hotokka. *Int. J. Quantum Chem.* **19,** 221 (1986).
12. H.-M. Xiao and M. Jiang. *Acta Chim. Sin.* **47,** 1164 (1989).
13. Y. Ling, Z.-H. Tang and H.-M. Xiao. *Propellants Explos. Pyrotech.* **17,** 116 (1992).
14. S. Odiot, M. Blain, J. M. Leclercq, J. Leclercq and S. Fliszar. *Propellants, Explos. Pyrotech.* **9,** 82 (1984).
15. H.-M. Xiao, J.-F. Fan and X.-D. Gong. *Propellants Explos. Pyrotech.* in press.

16. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart. *J. Am. Chem. Soc.* **107,** 3902 (1985).

17. J. J. P. Stewart, MOPAC. *a General Molecular Orbital Package, QCPE 455,* 5th ed. QCPE, Bloomington, IN. (1988).

18. J. A. Pople and D. L. Beveridge. *Approximate Molecular Orbital Theory.* McGraw-Hill, New York (1970).

19. K. B. Wiberg. *Tetrahedron* **24,** 1083 (1968)

20. P. K. Weiner. PhD, Dissertation, University of Texas at Austin, Tx (1975).