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EXPERIMENTAL AND THEORETICAL STUDYING THE THERMOLYSIS OF NITRATE

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This paper presents calorimeter measurement for the thermal decomposition of *n*-propyl nitrate (NPN), isopropyl nitrate (IPN) and 2-ethylhexyl nitrate (EHN). Similar experimental results of triethylene glycol dinitrate (tri-EGDN) and tetraethylene glycol dinitrate (tetra-EGDN) are included for comparison. The potential energy surfaces (PESs) along O–NO_2 bond stretch are investigated using the DFT (B3P86, B3PW91 and B3LYP), ab initio Hartree-Fock and PM3 methods. The good coincidence of experimental with theoretical results indicates that initial stage in the thermal decomposition of five nitrates is only unimolecular homolytical dissociation of the O–NO_2 bonds and the activation energies of thermolysis by DSC correspond to the energies of O–NO_2 bond scission of nitrates.

Keywords: *density functional theory (DFT), nitrate, potential energy surface (PES), thermolysis, unimolecular homolytical dissociation*

Introduction

Organic nitrates have been known since the early 1900s. The chemistry of organic nitrates began to be a significant research focus as far back as the 1930s. Comprehensive reviews are available on their use as additives to explosives and propellants. Since then, the organic nitrates to be in use as reactive species in other areas of science and technology have been investigated extensively [1–3].

In certain military explosives, additives such as nitrates have been used to sensitize the explosive mixture, making the mixture more easily to be ignited and to grow to detonation from hot spots such as are caused by sparks, flame, and other sources of heat and high temperature [4–6]. These nitrates are relatively unstable molecules, and their decomposition at low temperatures produces free radicals. The sensitizing effect of nitrates is attributed to the promotion of reaction kinetics via the formation of RO· and ·NO_2 radicals and their further bifurcation into smaller radicals and atoms. In fact, some nitrates, which contain oxygen in their molecular structure, can be considered monopropellants, which are generally known as low-sensitivity condensed explosives with relatively high vapour pressure [7]. The five acyclic nitrates selected for this study are *n*-propyl nitrate (NPN), isopropyl nitrate (IPN), 2-ethylhexyl nitrate (EHN), triethylene glycol dinitrate (tri-EGDN) and tetraethylene glycol dinitrate (tetra-EGDN). They are detonable liquid that may be chosen to serve as additive to military explosives.

Thermal stability and reliable thermodynamical data for quantitative predictions of chemical reactivity are required for design and application of nitrates in explosives. The knowledge of the thermal behaviors of O–NO_2 bond dissociation in nitrates is particularly important to understand the sensitizing mechanism and effect. In this work, thermal decomposition dynamics and behavior of five nitrates are evaluated using both theoretical and experimental methods.

Experimental

Methods

Ambient-pressure DSC experiments for the exothermic decompositions of compounds IPN, NPN and EHN were carried out with Mettler DSC822^e, using a sealed cell made of an aluminum cell with a rolled-up side. The amount of samples was about 0.2 mg. The scan rate was 20° min^{-1}, and the temperature range was 40–350°C. Chen *et al.* [8] and Oxley *et al.* [9] performed similar ambient-pressure DSC experiments on tri-EDGN and tetra-EDGN, respectively.

Computational methods

The calculations were performed with the Gaussian 98 program package [10]. For the density functional theory (DFT) [11, 12] calculations, we used a variety of

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functionals, namely B3LYP [13], B3PW91 [14, 15] and B3P86 [13, 16], as well as the Hartree–Fock calculation [17], all with the 6–311+G(d) basis set [18, 19]. These computations also were performed using the semi-empirical methods such as PM3 [20].

Geometry optimization was conducted without any constraint. Each optimized structure was confirmed by the frequency calculation to be the real minimum without any imaginary vibration frequency. Then the optimal conformation from the search was used as the starting geometry for scanning the potential energy surface (PES) of each title compound. Adiabatic PES along the O–NO_2 bond stretch were calculated, with a 0.05 Å step size from ~1.20 up to 2.30 Å. PES scans for five acyclic nitrates used the guess=(always, mix) option to allow for unrestricted calculations needed for appropriate dissociation limits.

Results and discussion

O–NO_2 bond lengths in five nitrates

The O–NO_2 bond lengths in NPN, IPN, EHN, tri-EGDN and tetra-EGDN calculated using the various levels of theory and 6-311+G* basis set are presented in Table 1. The B3P86/6-311+G* structures are depicted in Fig. 1 together with the corresponding O–NO_2 bond lengths.

For the O–NO_2 bond distances of five title compounds, although there are no experimental data for comparison, we find that the B3P86 calculation results are in excellent agreement with the B3PW91 bond distances. So the results obtained via B3P86/6-311+G* and B3PW91/6-311+G* are utilized to the following analysis. The O–NO_2 bond lengths in NPN, IPN, EHN, tri-EGDN and tetra-EGDN calculated from B3P86/6-311+G* are 1.400, 1.397, 1.402, 1.406 and 1.405 Å, respectively. The corresponding values via B3PW91/6-311+G* are 1.402, 1.400, 1.405, 1.408 and 1.407 Å, respectively. It is well-known that for the same type bond, the shorter the bond length is, the stronger the bond is, and vice versa. It is obvious that among five nitrates, O–NO_2 bond of IPN is shortest, O–NO_2 bond of tri-EGDN is longest. The O–NO_2 bond lengths from three DFT methods (B3P86, B3PW91 and B3LYP) calculations suggest that the order of O–NO_2 bond strengthen in five nitrates are in the following order: IPN>NPN>EHN>tetra-EGDN>tri-EGDN.

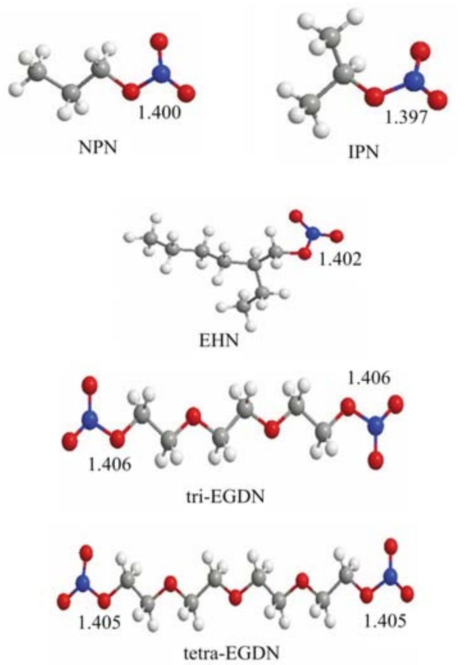

Fig. 1 B3P86/6-311+G* optimized structures of five nitrates. Bond distances in Å

Potential energy surface

The energetic profile of a bond-breaking process can be best described by the PES along the bond. For the O–NO_2 bond breaking of five nitrates, a full investigation of the PESs renders a clear picture of the energetics of bond fragmentation. The potential energy curves of five title compounds investigated with various methods are plotted in Fig. 2. The relative energy (ΔE) is calculated by the difference of the energy of the geometry at each point on the PES minus that of optimized molecular structure.

The potential energy surfaces (PESs) are crucial to understanding the decomposition mechanism. Comparison of curves for five nitrates shows that the potential energy minima all occur at R(O–NO_2) values of 1.35, 1.40, 1.40 and 1.40 Å, for UHF/6-311+G*,

Table 1 Equilibrium O–NO_2 distance of five nitrates (Å)

r_e(O–NO_2)	Compounds				
	NPN	IPN	EHN	tri-EGDN	tetra-EGDN
HF/6-311+G*	1.327	1.326	1.327	1.330	1.329
B3P86/6-311+G*	1.400	1.397	1.402	1.406	1.405
B3PW91/6-311+G*	1.402	1.400	1.405	1.408	1.407
B3LYP/6-311+G*	1.416	1.414	1.419	1.422	1.421
PM3	1.482	1.475	1.521	1.505	1.503

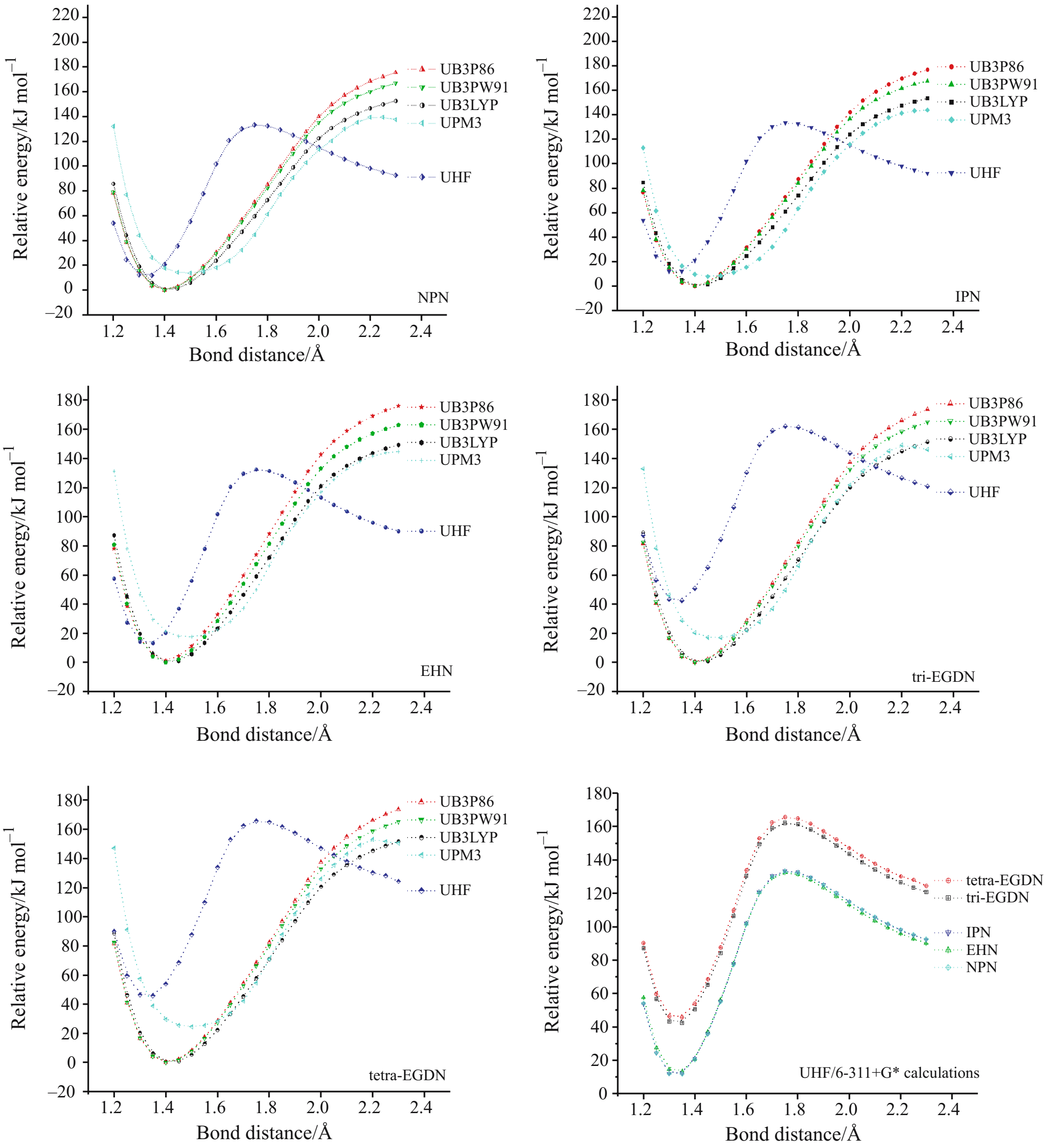

Fig. 2 Potential energy surfaces of five nitrates along the R (O–NO_2) coordinate

UB3P86/6-311+G*, UB3PW91/6-311+G* and UB3LYP/6-311+G* calculations, respectively. Comparing to Table 1, one can see that these values are in line with the O–NO_2 bond lengths of optimized geometries at each calculation level. Similar cases happened on those of UPM3 theory. However, from calculations of three DFT and UPM3 methods, the potential energy curve of each nitrate rises monotonically beyond the O–NO_2 equilibrium distance. This is an illogical phenomenon. As we know, in the process of homolytic bond dissociation, the adiabatic PES has a maximum ΔE value that suggests cleavage of O–NO_2 bond requires the least energy. The PESs of five nitrates from UHF/6-311+G* calculations are reasonable.

To make the comparison of the curves more quantative, the potential energy surfaces of five nitrates at UHF/6-311+G* level are singled out to depicted in one picture, the last in Fig. 2 and the ΔE values for the PESs at each point are tabulated in Table 2. On the whole, the PESs of five title compounds along the O–NO_2 bonds are similar and follow the typical Morse potential shape, in that each of the surfaces has only one minimum at R(O–NO_2)=1.35 Å and the relative energy increases monotonically as O–NO_2 bond is stretched to 1.75 Å, then decreases. The last picture of Fig. 2 shows that the potential energy curve of EHN is extremely close to the corresponding ones of NPN and IPN, and the potential energy curves of tri-EGDN and tetra-EGDN are also extremely close to each other. As stated above, the PES has one minimum at R(O–NO_2)= 1.35 Å indicates that the equilibrium O–NO_2 distance in five nitrates from UHF/6-311+G* calculation is in the vicinity of 1.35 Å. The maximum of ΔE value lies in R(O–NO_2)=1.75 Å implies that when the O–NO_2 bond is stretched to 1.75 Å, the bond is essentially rup-

Table 2 Calculated relative energy (kJ mol^{-1}) on PESs along O–NO$_2$ bond stretch of five nitrates with UHF/6-311+G* method

Bond distance/Å	NPN	IPN	EHN	tri-TEGDN	tetra-TEGDN
1.20	54.03	53.64	57.50	90.14	87.15
1.25	24.47	24.34	27.43	59.63	56.56
1.30	11.97	12.05	14.46	46.40	43.22
1.35	11.87	12.07	13.28	45.66	42.43
1.40	20.61	20.90	20.32	53.91	50.63
1.45	35.63	36.00	36.88	68.56	65.22
1.50	55.03	55.42	55.92	87.67	84.29
1.55	77.35	77.77	77.92	109.80	106.37
1.60	101.50	101.97	101.81	133.83	130.39
1.65	120.43	120.90	120.38	152.94	149.48
1.70	129.89	130.33	129.49	162.45	158.95
1.75	133.09	133.50	132.37	165.62	162.13
1.80	132.33	132.72	131.35	164.83	161.32
1.85	129.23	129.57	128.02	161.66	158.14
1.90	124.87	125.10	123.39	157.19	153.68
1.95	119.93	120.09	118.28	152.21	148.64
2.00	114.92	114.99	113.08	147.11	143.54
2.05	110.09	110.08	108.09	142.20	138.66
2.10	105.65	105.54	103.52	137.71	134.14
2.15	101.66	101.47	99.40	133.67	130.07
2.20	98.143	97.88	95.77	130.10	126.50
2.25	95.12	94.78	92.65	128.09	123.43
2.30	92.55	92.13	90.00	124.37	120.78

tured. According to Table 2, at the UHF/6-311+G* level, the least energies required for cleavage of the O–NO$_2$ bonds in NPN, IPN, EHN, tri-EGDN and tetra-EGDN are 133.09, 133.50, 132.37, 162.13 and 165.62 kJ mol^{-1}, respectively.

Analysis of experimental and theoretical results

DSC measurements have wide application in studying the decomposition kinetics of compound or complex [21–24]. In this paper, the kinetic parameters such as activation energies of five nitrates were obtained from the calculation of a single DSC curve by the integral, differential and exothermic rate equations. They are 135.0, 124.9, 131.5, 143.8 and 148.0 kJ mol^{-1} for NPN, IPN, EHN, tri-EGDN and tetra-EGDN, respectively. Theoretically, from Table 2 and the last picture of Fig. 2, the potential energy surfaces calculated at the UHF/6-311+G* level quantatively give the result that the rupture of the O–NO$_2$ bonds in NPN, IPN, EHN, tri-EGDN and tetra-EGDN needs least energy of 133.09, 133.50, 132.37, 162.13 and 165.62 kJ mol^{-1}, respectively. The least difference between activation energies and O–NO$_2$ bond dissociation energies is 0.87 kJ mol^{-1} for EHN, and the largest one is 18.33 kJ mol^{-1} for tri-EGDN. This coincidence can be considered as very satisfactory especially if one keeps in mind that full agreement between the calculated and experimental data is impossible. A certain degree of agreement in this case implies that the calculation and experiment similarly reproduce the tendencies of variation of dissociation energy for O–NO$_2$ bonds in five nitrates.

It is obviously that the observed activation energies for decomposition of examined nitrates falls in a range comparable to the O–NO$_2$ bond energy. The bond dissociation energy (BDE) is an ambiguous notion, which can be formulated differently [25]. In this study, the method to determine BDE from scanning the potential energy surface along O–NO$_2$ bond stretch is an inexpensive way of quantum-chemical calculations, which neglect radical optimization and the occupancies of the vibrational energy level. As a whole, the best coincidence of the experimental values of activation energy with the theoretical ones of least energy required for cleavage of the O–NO$_2$ bonds for the five examined nitrates clearly shows that the initial stage in the thermal decomposition of five title compounds is only unimolecular homolytical dissociation and the activation energies correspond to the BDEs of the O–NO$_2$ bonds.

Conclusions

In the present paper, we undertake a systematic study of the O–NO_2 bond dissociation in NPN, IPN, EHN, tri-EGDN and tetra-EGDN from experimental and theoretical methods. The thermodynamical parameters such as activation energies and rate constants on the thermal decomposition of five nitrates were analyzed by using DSC. Also, the thermal decomposition behaviors of O–NO_2 bond in five nitrates were investigated by employing the PESs. The PESs along O–NO_2 bond distance increasing of all five nitrates show that the typical and reasonable surface expected for homolytic bond dissociation is the one from UHF/6-311+G* calculations, which has only one minima and maximum potential energy. Base on the analysis of the experimental and theoretical results, we can draw a conclusion that the observed activation energies for thermolysis correspond to the O–NO_2 bond dissociation energies of five nitrates. That the activation energies agree rather well with BDEs of O–NO_2 bonds strongly suggests a radical mechanism of thermal decomposition with initial homolytic dissociation of the O–NO_2 bond, which is typical of acyclic nitrates. From the findings discussed above, we may conclude that combining quantum theoretical calculation with application of calorimeter techniques is a promising tool to study the thermal decomposition of nitrate systems. This paper opens new lines of thought in our standing of thermal decomposition dynamics and behavior of five nitrates.

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