

APPLICATION OF HIGHLY ACCURATE QUANTUM CHEMISTRY APPROACH FOR THE STUDY OF THERMOCHEMISTRY OF N,O-CONTAINING HIGH-ENERGY COMPOUNDS

V. G. Kiselev^{1,2} and N. P. Gritsan^{1,2}

¹Institute of Chemical Kinetics and Combustion
Siberian Branch of the Russian Academy of Sciences
Novosibirsk, Russia

²Novosibirsk State University
Novosibirsk, Russia

Highly accurate quantum chemistry procedures have been applied for the calculating thermodynamic and kinetic properties of a number of N,O-containing high-energy compounds. It has been found that only G3 procedure gave accurate results (within 1 kcal/mol) for the formation enthalpy of nitroalkanes, their isomers, and radical products. This procedure was used to calculate the standard-state formation enthalpy of a new promising high-energy compound — furazano-1,2,3,4-tetrazine-1,3-dioxide. Furthermore, the primary reactions in thermolysis of 5-aminotetrazole (5-ATZ) and hydrazinium nitroformate (HNF) were studied theoretically in both gas phase and melt using a simplified model of the latter. The influence of the melt on the rate constants of elementary reactions was taken into account by calculating the solvation free energies using a polarizable continuum solvation model (PCM). It was concluded that thermolysis of 5-ATZ cannot be satisfactorily described by the mechanisms proposed in the literature and reactions in the H-bonded complexes should be taken into account. Hydrazinium nitroformate was found to decompose preferably to nitroform and hydrazine in both gas phase and melt. Hydrazinium nitroformate decomposition occurs mainly through the intermediacy of nitroform, the computations do not support the suggestion that the aci-form is an important intermediate of HNF thermolysis.

Introduction

Thermodynamics and rate constants of elementary reactions are crucial for deep understanding and modeling physical and chemical phenomena taking place during the combustion process. Detailed chemical mechanisms of combustion of energetic materials are very complicated and usually contain hundreds of elementary reactions. However, the experimental data are lacking for most of elementary reactions.

It is difficult to evaluate experimentally the rate constants of elementary reactions due to a significant number of fast simultaneous processes in the crystalline, melt, and gas phase with numerous short-lived intermediates involved. Moreover, the kinetic measurements are sometimes hindered by experimental difficulties in the detection of some intermediates and nonisothermal experimental conditions. As a result, reliable experimental data are usually available for only a small number of known reactions.

At present, quantum chemical calculations are the most appropriate alternative for obtaining thermodynamic and kinetic properties of elementary reactions. All the data (electronic energy levels of the reactants, products and transition states, normal frequencies, etc.) necessary for the calculations of gas-phase enthalpies of formation ($\Delta_f H_{\text{gas}}^0$), reaction enthalpies ($\Delta_r H^0$), activation barriers and rate constants can be obtained from the first principles (*ab initio*) by means of quantum chemical calculations.

In the present paper, the progress in application of modern highly accurate quantum chemical procedures for more precise calculations of the thermodynamic and kinetic properties of some promising high-energy compounds is described. The attention is focused on the calculations of enthalpy and rate constants of primary reactions. Apart from the traditional study of gas-phase reactions, the processes in the melt are considered using a simplified model of the latter. The same reactions were considered to proceed in the gas phase and in the melt, and the influence of the melt on the rate constants was taken into account by calculating the solvation free energy. Moreover, some bimolecular reactions of the species under study which might be especially important in the melt were also considered.

Three promising high-energy compounds were closely scrutinized. The first one, 5-ATZ, is of significant interest for combustion chem-

istry as a burning rate modifier and fire suppressor. Due to its thermal stability, nonexplosive character, and high nitrogen content, 5-ATZ is an environmentally friendly gas-generator agent [1, 2]. The second compound, $[\text{C}(\text{NO}_2)_3]^-[\text{N}_2\text{H}_5]^+$ (HNF), a salt of hydrazine (N_2H_4) and nitroform ($\text{CH}(\text{NO}_2)_3$), is of significant interest as a component of promising high-performance solid rocket propellants and environmentally "clean" chlorine-free oxidizer. The third species of interest, [1,2,5]oxadiazolo[3,4-*e*][1,2,3,4]tetrazine-4,6-di-*N*-dioxide (furazano-1,2,3,4-tetrazine-1,3-dioxide, FTDO), is a promising oxidizer synthesized in Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences [4].

Even though thermal decomposition of 5-ATZ and HNF has been intensively studied under different conditions, there are still some contradictory assumptions concerning the primary reactions and key intermediates of their thermolysis. Thermal decomposition of FTDO has never been studied, and even the data on its formation enthalpy are contradictory.

Computational Details

All thermochemical data as well as barriers of unimolecular reactions of different 5-ATZ and HNF isomers have been calculated using the multilevel G3 procedure [4]. This procedure was used since the present authors have demonstrated earlier its good performance for thermochemical calculations in C, N, O containing systems [5]. The B3LYP/6-311G(*d,p*) [6] method has also been employed in the cases when application of G3 procedure was excessively time and resource consuming. The free energies of solvation were calculated using the PCM model [7] at the B3LYP/6-311G(*d,p*) level of theory [6]. All quantum chemical computations were performed using Gaussian 03 [8] suite of programs.

The gas phase enthalpies of formation (at $p = 1$ atm and $T = 298$ K, $\Delta_f H_{\text{gas}}^0$) were calculated using the atomization energy approach: the calculated atomization energies at 298 K were subtracted from the well-known enthalpies of formation of isolated atoms.

The influence of the melt on thermochemistry and rate constants was taken into account by the calculation of the free energies of solvation. Aniline, a typical aromatic amino-compound, was chosen as a

solvent in present model calculations for 5-ATZ system and acetonitrile, a typical polar solvent, was used in the case of HNF. Apart from the usage of this simplified model, some bimolecular reactions, which could easily proceed in the melt were considered.

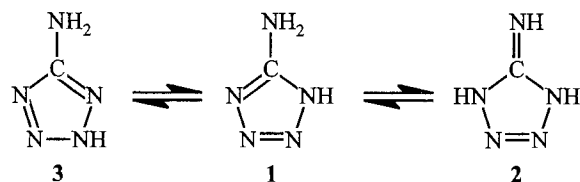
The rate constants of monomolecular reactions in the gas phase at a high pressure limit and in the melt were computed in accordance with the canonical transition state theory (TST).

Results and Discussion

A series of multilevel (G2, G3, G2M(CC5)) and DFT-based methods (B3LYP, MPW1B95, MPWB1K) have been used previously to calculate thermodynamic properties of nitroalkanes [5]. It was demonstrated that only the G3 procedure gave accurate (within 1 kcal/mol) results for the formation enthalpy of nitroalkanes, their isomers and radical products calculated using the atomization energy approach. Therefore, G3 procedure was chosen as a main method of calculations in this study.

Only monomolecular reactions of 5-ATZ were considered previously in the analysis of its thermolysis. However, it is clear that 5-ATZ in all isomeric forms could form hydrogen-bonded complexes. Therefore, along with monomolecular reactions, the reactions in the selected H-bonded complexes were analyzed. On the basis of present calculations, some interesting features of 5-ATZ thermal decomposition were revealed. It was found that the iminoform **2** is prone to the fast bimolecular transformation to more thermodynamically favorable amino isomer **1** (Scheme 1). Thus, in contrast to previous assumptions [9, 10], the calculations suggest that the iminoform **2** is not important in the chemistry of 5-ATZ decomposition in both melt and gas phase and 5-ATZ exists mainly in the thermodynamically more preferable **1** and **3** forms.

The N_2 elimination reaction was found to be the dominant unimolecular channel of the amino and 2H isomer decomposition in the gas phase. The account of the melt by means of simple PCM does not change this tendency. Though only selected H-bonded dimers of these compounds and their reactions were considered, new important channels of decomposition involving intermolecular hydrogen transfer



Scheme 1 Different forms of 5-ATZ

have been found. The barriers of these new reactions are lower than the barriers of the monomolecular processes considered previously. In agreement with the existing experimental data [9, 10], HN_3 elimination dominates for some of considered complexes.

Therefore, one can conclude that the initial stages of thermolysis of 5-ATZ cannot be satisfactorily described by the simple unimolecular reactions proposed in the literature. A correct description can be attained only by account of formation of H-bonded complexes and their subsequent decomposition in both the gas phase and melt.

The primary reactions of the thermal decomposition of HNF, as well as ammonium nitroformate (ANF), were also investigated theoretically using G3 multilevel procedure. Calculations were performed for the reactions in the gas phase and in the melt. The influence of the melt on the reaction barriers was taken into account by calculation of the solvation free energies using a PCM and acetonitrile as a solvent.

In contrast to many other energetic salts, the ionic salt structures of the HNF and ANF were found to be minima on the PES. Although a shallow minimum corresponding to ionic salt exists on the PES of HNF, the activation barriers of its transformation are quite low. The energetically favorable structures of the HNF and ANF in the gas phase are the H-bonded complexes.

In both the gas phase and melt, the HNF decomposes preferably to nitroform **1** and hydrazine **3**. The activation energy of this reaction was found to be less than 10 kcal/mol. This fact agrees well with the experimentally observed absence of HNF among the gas phase decomposition products [11–13]. The thermolysis of HNF occurs mainly through the intermediacy of nitroform, the computations does not support the previously made suggestions [12, 13] that the aci-nitroform $\text{C}(\text{NO}_2)_2\text{NOOH}$ is an important intermediate of HNF decomposition.

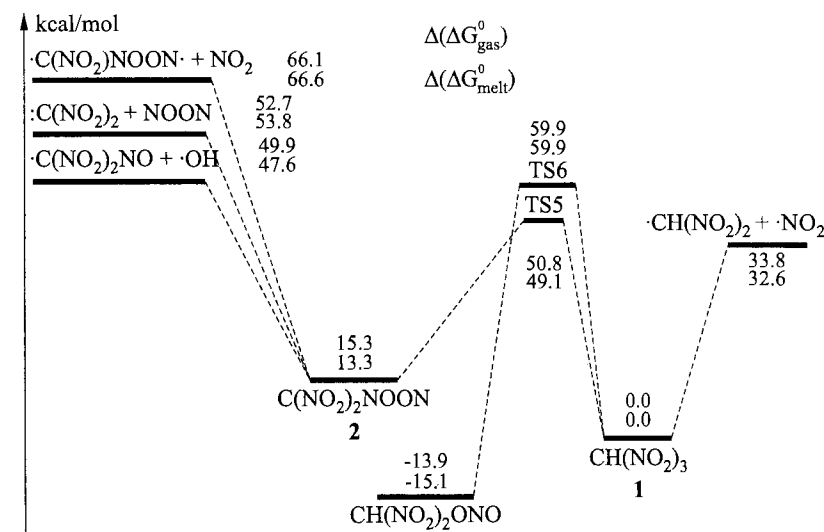


Figure 1 Relative Gibbs free energies at 298 K in the gas phase ($\Delta(\Delta G_{\text{gas}}^0)$) and melt ($\Delta(\Delta G_{\text{melt}}^0)$) for the stationary points on the PES of **1** and **2**. All values are in kcal/mol

The C–NO₂ bond cleavage was found to be the dominant reaction of the subsequent nitroform decay (Fig. 1).

References

1. Stoner, C., Jr., and T. Brill. 1991. Thermal decomposition of energetic materials. 46. The formation of melamine-like cyclic azines as a mechanism for ballistic modification of composite propellants by DCD, DAG, and DAF. *Combust. Flame* 83:302–8.
2. Williams, G., S. Palopoli, and T. Brill. 1994. Thermal decomposition of energetic materials. 65. Conversion of insensitive explosives (NTO, ANTA) and related compounds to polymeric melon-like cyclic azine burn-rate suppressants. *Combust. Flame* 98:197–204.
3. Churakov, A. M., S. L. Ioffe, and V. A. Tartakovskii. 1995. Synthesis of [1,2,5]oxidiazolo[3,4-e][1,2,3,4]tetrazine 4,6-Di-N-oxide. In: *Mendeleev Communications*. 227–28.

4. Curtiss, L., K. Raghavachari, P. Redfern, V. Rassolov, and J. Pople. 1998. Gaussian-3 theory for molecules containing first and second-row atoms. *J. Chem. Phys.* 109:7764–76.
5. Kiselev, V., and N. Gritsan. 2008. Theoretical study of the nitroalkane thermolysis. 1. Computation of the formation enthalpy of the nitroalkanes, their isomers and radical products. *J. Phys. Chem. A* 112:4458–64.
6. Becke, A. 1993. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 98:5648–56.
7. Cancès, M., B. Mennucci, and J. Tomasi. 1997. A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics. *J. Chem. Phys.* 107:3032–39.
8. Frisch, M., G. Trucks, *et al.* 2004. Gaussian 03, Rev. C.02, Gaussian, Inc., Wallingford CT.
9. Lesnikovich, A., O. Ivashkevich, S. Levchik, A.I. Balabanovich, P.N. Gaponik, and A.A. Kulak. 2002. Thermal decomposition of aminotetrazoles. *Thermochimica Acta* 388:233–51.
10. Paletsky, A., N. Budachev, and O. Korobeinichev. 2009 (in press). The mechanism and kinetics of the 5-aminotetrazole thermal decomposition. *Kinet. Katal.* 50(5).
11. Williams, G., and T. Brill. 1995. Thermal decomposition of energetic materials. 67. Hydrazinium nitroformate (HNF) rates and pathways under combustionlike conditions. *Combust. Flame* 102:418–26.
12. Louwers, J., T. Parr, and D. Hanson-Parr. 1999. Decomposition and flame structure of hydrazinium nitroformate. AIAA Paper No. 99-1091.
13. Sinditskii, V., V. Serushkin, S. Filatov, and V. Egorshv. 2000. Flame structure of hydrazinium nitroformate. *5th Symposium (International) Special Topics in Chemical Propulsion Proceedings*. Eds. K. K. Kuo and L. T. De Luca. Stresa, Italy. 576–86.

EFFECT OF LOW TEMPERATURE GLOW DISCHARGE PLASMA ON SURFACE NANORELIEF OF 1,3,5,7-TETRANITRO-1,3,5,7- TETRAAZACYCLOOCTANE PARTICLES

A. P. Korobko, S. V. Krashennnikov, S. N. Drozd,
and I. V. Levakova

State Scientific Center of Russian Federation
“L. Ya. Karpov Institute of Physical Chemistry”
Moscow 105064, Russia

The influence of air glow discharge plasma on surface nanorelief (surface morphology) of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane particles was studied. Changes in morphology were estimated quantitatively by the help of surface fractal dimension D_S . A method of differential scanning calorimeter was employed for determining surface fractal dimensions.

Introduction

Cyclic eight-membered 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (TNCO) is a crystalline low molecular weight organic product. At about 180–190 °C, TNCO has crystal–crystal phase change from stable at room temperature β -polymorph to δ -polymorph.

Powdered TNCO as a thermally stable explosive has found considerable practical use, in particular, as one of the main components of polymer energetic condense systems (PECS). Efficiency of TNCO application in PECS is dependent not only on its chemical nature but on its surface properties as well.

Glow discharge plasma treatment of powdered TNCO in nonpolymerizing gases leads to the formation of a layer of products enriched with oxygen and nitrogen-containing functional groups on the surface