The chemistry of 3-nitro-1,2,4-triazol-5-one (NTO): thermal decomposition

Henric Östmark [a,1], Helena Bergman [b] and Göran Åqvist [b]

[a] *Department of Physical Chemistry, Royal Institute of Technology, S-100 44 Stockholm (Sweden)*
[b] *National Defence Research Establishment, S-172 90 Sundbyberg (Sweden)*

Abstract

This paper presents the results from a study of the thermal decomposition and thermal stability of NTO (3-nitro-1,2,4-triazol-5-one). Mass spectra of NTO are presented (electron impact 20 and 70 eV and chemical ionisation spectra). The large abundance of the molecular ion in these spectra shows that NTO is a more stable molecule than TNT or RDX. The data acquired for NTO is summarised as a proposed mass spectral fragmentation path. A number of laser ignition measurements were conducted. These measurements showed a strong pressure dependence, which clearly indicates a multiple phase (condensed and gas phase) ignition. The laser ignition measurements also showed that the sensitivity to ignition is slightly higher than that for TNT. The results of the LI-MS (laser induced mass spectrometry) method applied to NTO imply that the probable decomposition path is an elimination of NO_2 followed by a breaking of the azole ring. The chemiluminescence (CL) method was used for determination of the activation energy and the frequency factor ($E_a = 140$ kJ and $K_0 = 5 \times 10^6$ s^{-1} in the temperature interval 100–140°C). Chemilumines- cence data for RDX and TNT was acquired for comparison. The DSC spectrum of NTO showed only one peak, a very strong exothermic peak at 253°C. This study is complemented with some quantum mechanical calculations which were conducted in an attempt to verify the initial steps in the decomposition path and to explain the high stability of NTO. The results were computed with the MOPAC 6.0 code using the semi-empirical modified neglect of diatomic overlap (MNDO) method with the parametric method 3 (PM3) parameter set at the unrestricted Hartree–Fock level.

INTRODUCTION

In the search for new and safer high explosives the nitroazoles have been identified as a possibly interesting class in addition to nitroaromatics (e.g. trinitrotoluene, TNT) and nitroamines (e.g. octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, HMX). One of these identified candidates

---

is NTO (3-nitro-1,2,4-triazol-5-one), which is a new and very interesting explosive with high performance (about 80% of that of hexahydro-1,3,5-trinitro-1,3,5-triazine, RDX) and low sensitivity (less than that of TNT). A great deal of sensitivity and performance data on NTO has been published: detonation velocity [1], Chapman–Jouquet (CJ) pressure [1], spark sensitivity [1], impact sensitivity [1] and friction sensitivity [2]. An extensive review of the chemistry of nitroazoles can be found in ref. 3. The vacuum stability of NTO has been examined by Lee et al. [1]. Quantum mechanical (QM) studies of NTO can be found in refs. 4–6. A literature survey on NTO has also been published [7], but very little has been reported about its thermal sensitivity [8] and its decomposition [9]. In order to analyse the thermal sensitivity of a high explosive, it is necessary to be aware that the thermal sensitivity can be divided into at least three different regimes; molecular sensitivity, decomposition sensitivity and the sensitivity to starting a self sustained reaction. In this paper all three regimes are examined: the molecular sensitivity by mass spectroscopy, the thermal stability by DSC and chemiluminescence (CL), the thermal decomposition path by laser induced mass spectrometry (LI-MS) and the sensitivity to a self-sustained reaction by a laser ignition method. In addition, some initial quantum mechanical studies on the molecular stability are presented. The final part of this paper is devoted to a proposed decomposition pathway.

MATERIALS AND METHODS

Explosives

The NTO used in our experiments was synthesised by the Chipen method [10], which is a two-step synthesis. The first step is the formation of 1,2,4-triazole-5-one (TO) by condensation of semicarbazide hydrochloride and formic acid. The second is the nitration of the TO with nitric acid. The synthesised NTO was purified by several recrystallisations from water. The purity of the NTO was then measured by a HPLC method [9]. These analyses showed that the purity of the NTO was greater than 99%. The chemical analysis was conducted on a Waters HPLC equipped with a four wavelength detector (Waters 490). The data was collected and analysed with the Baseline 810 computer program (PC based). It was very difficult to achieve a good separation of the NTO–TO mixture. This difficulty forced us to use a solvent containing counter-ions (TBA, tetrabutylammonium phosphate) for the separation.

Mass spectroscopy

The thermal fragmentation of RDX shows similarities to its mass spectral fragmentation [11]. A mass spectroscopic study is thus the natural
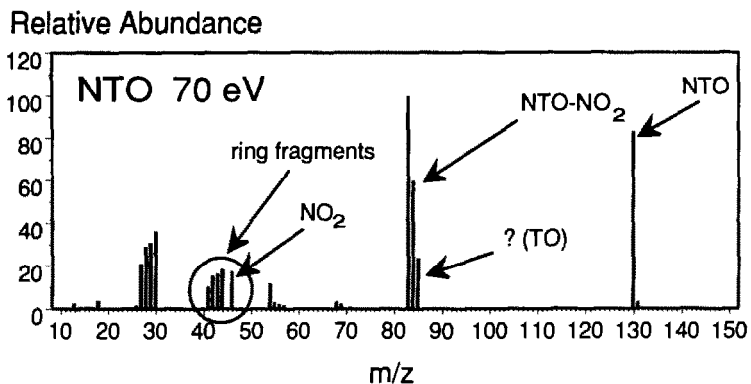
Relative Abundance

Fig. 1. Mass spectrum for NTO.

starting point for acquiring some information about the decomposition mechanism. The mass spectroscopic study was conducted on a JEOL 300D double focusing magnetic sector instrument equipped with a PC based computer system with Technivent Vector/2 software for data analysis. All mass spectra were acquired by using the solid sample inlet on the mass spectrometer with a heating rate of about 50°C min^{-1}. Both electron impact (EI) (20 and 70 eV) and chemical ionisation (CI) spectra were acquired. The CI spectra were obtained by using methane as the reagent gas. Figure 1 shows the mass spectrum for NTO. This spectrum consists of three characteristic parts: the molecular ion (m/z 130), the group at m/z 83, 84 and 85 (the azole ring) and the azole ring fragment group (m/z 41, 42, 43 and 44). The fact that the molecular ion (m/z 130) is found in relatively large amounts in the EI spectrum (70 eV) indicates
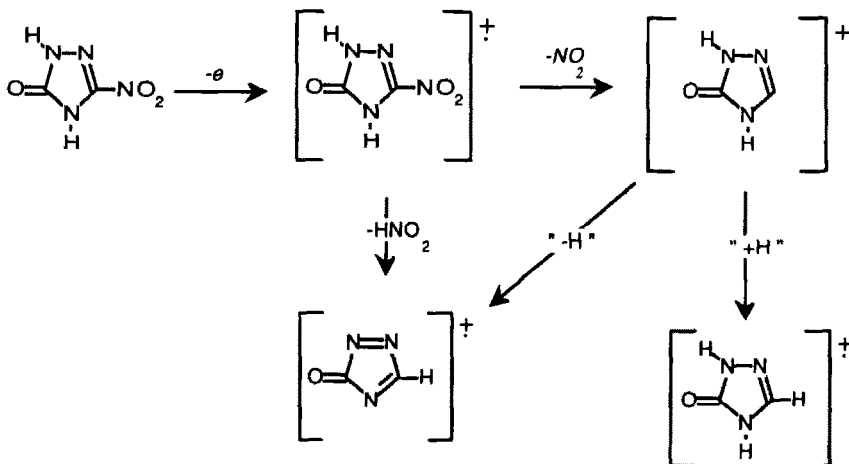

Fig. 2. Mass spectral fragmentation of NTO.

that the NTO molecule is very stable compared with HMX, RDX and TNT, where only TNT exhibits a molecule ion and then only a weak one [12]. The CI spectrum of NTO shows two peaks at m/z 131 and m/z 261 (2M + 1); the m/z 261 peak is probably a cluster ion (adduct). The mass spectrum for TO (EI 70 eV) consisted of only two peaks, at m/z 42 and 85. In Figure 2 is shown a proposed mass spectral fragmentation of NTO. The reactions involving a hydrogen exchange should be regarded as parts in a composite reaction and not as single reactions. The most likely route is ion–molecule reactions involving either HNO_2 or the $C_2H_2ON_3$ fragment.

Laser ignition

The sensitivity to a self-sustained reaction must take into account the chemical kinetics as well as energy and mass transport processes. To test the importance of any gas phase processes and to measure the pure thermal sensitivity of NTO to a self-sustained reaction, a series of laser ignition measurements was conducted. The laser ignition method used is fully described in ref. 14. The set-up is the same as shown in Fig. 4 (below) except that the capillary column and the mass spectrometer are not present. The measurements were performed in the following way. The cw laser beam was focused through a window in the explosive chamber on to the high explosives, and the degree of reaction was then measured by a photodiode. From these recordings the time to ignition, which is clearly distinguished by a sharp break upwards in the emitted light curve, was then measured. In Fig. 3 the time to ignition as a function of gas pressure
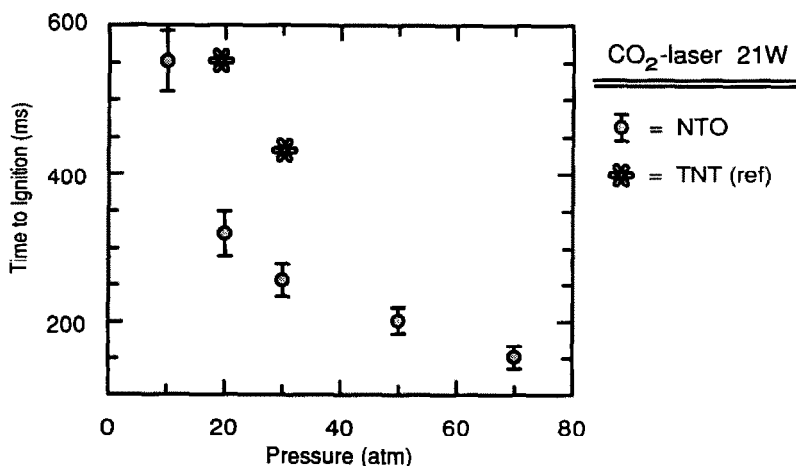

Fig. 3. Laser ignition of NTO: time to ignition vs. pressure. The error bars show the 90% confidence interval.

for a laser power of 21 W (CO_2 laser) can be seen. The strong pressure dependence found clearly indicates a multiple phase [14] (condensed and gas phase) ignition. For comparison, some TNT ignition data is also shown in Fig. 3. Neither the data for NTO nor the TNT ignition data are corrected for reflectivity. These measurements show that the sensitivity of NTO to a self-sustained reaction is slightly larger than for TNT but much less than that of RDX [14].

LI-MS

In order to get a better understanding of the pure thermal decomposition mechanism of NTO, the laser induced mass spectrometry (LI-MS) method [15, 16] was used. This method cannot distinguish between reactions in different interacting phases because the capillary is placed in the ignition zone and collects products for all participating phases. However, the purpose of these measurements is to find out which products are formed in the initiation process of NTO. For pure decomposition path studies other methods are better, e.g. STMBMS [17] or infrared multiphoton dissociation in a molecular beam [18]. The experimental set-up for LI-MS is shown in Fig. 4. The LI-MS equipment consists of an explosive chamber, a 180 W CO_2 continuous wave laser (Edinburgh PL 6) used to heat and hereby start a decomposition/ignition of the high explosive, and a mass spectrometer (JEOL 300D double focusing magnetic sector instrument equipped with a Vector/2 PC based
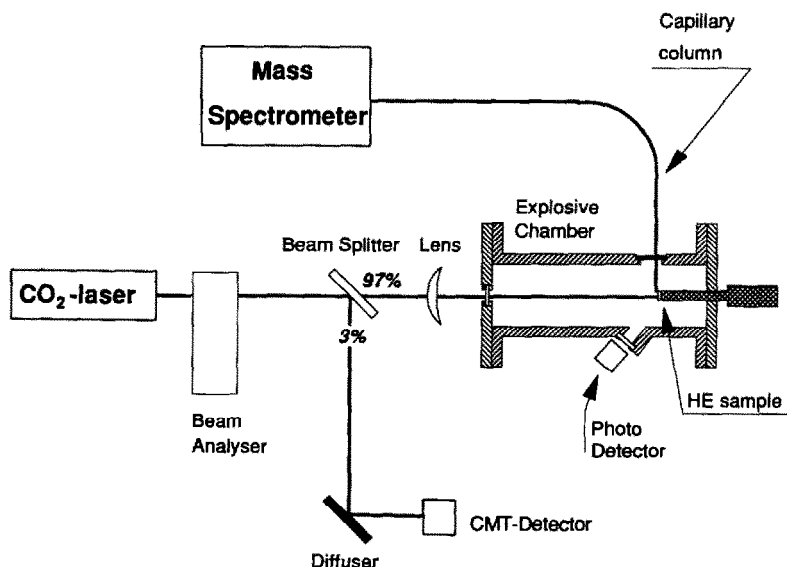

Fig. 4. LI-MS set-up.

computer system) for analysing the decomposition/reaction products. As interface between the reaction chamber and the mass spectrometer, a deactivated (and thus nearly chemically inert) fused silica capillary was used. One end of the capillary ends in the reaction zone and the other end terminates in the ionisation chamber in the mass spectrometer. The use of a capillary also enabled the use of increased pressure in the explosive chamber, up to 2.5 MPa. About 300 mg of NTO was pressed to a pellet of 10 mm diameter and a thickness of 2 mm. The density of the pellet was 95% of theoretical maximum density. The pellet was fastened to the sample holder by double-sided adhesive tape and placed in the explosive chamber. The sample holder was rotated for each laser pulse so that unreacted explosive was exposed to the laser beam. The capillary was connected to the explosive chamber by a capillary fed through and maintained in position by a fixing device.

The LI-MS total ion current (TIC) spectra consist of at least three peak groups. The first peak group (a small one) in the TIC spectrum consists of the mass numbers 46 (NO_2), 83, 84, 85 (the azole ring) and 42, 43, 44 (azole ring breakdown products). The m/z 42, 43 and 44 masses are also found in the second peak group (the large one) but here we also find m/z 52 and others. The possible assignments for these m/z values can be seen in Table 1. The molecular fragments with m/z 41, 42, 43 and 44 derive from the breakdown of the azole ring. The m/z 44 peak can also derive from the formation of CO_2. As the pulse power of the CO_2 laser was decreased and the ionisation voltage lowered from 70 to 20 eV these fragments became less significant. This was done to prevent the decomposition from going much further than the initial steps.

TABLE 1

NTO decomposition peaks and possible assignments (selected masses)

| m/z	Assignment	Strength	Comments
26/27	HCN	2	A lot of CN was also found by emission spectroscopy [13]
30	e.g. NO, H_2O	1	Mixed decomposition products
41	CN_2H	2	Azole ring fragment
42	CN_2H_2	1	Azole ring fragment
42/43	HOCN or OCNH	1	
44	CO_2, H_2NOC, (N_2O)	2	Carbon dioxide Azole ring fragment?
46	NO_2	2	Indicates NO_2 elimination from the ring
52	N_2C_2	3	?
83	C_2HN_3O	3	NTO HNO_2
84	$C_2H_2N_3O$	4	NTO NO_2
85	$C_2H_3N_3O$	4	TO?
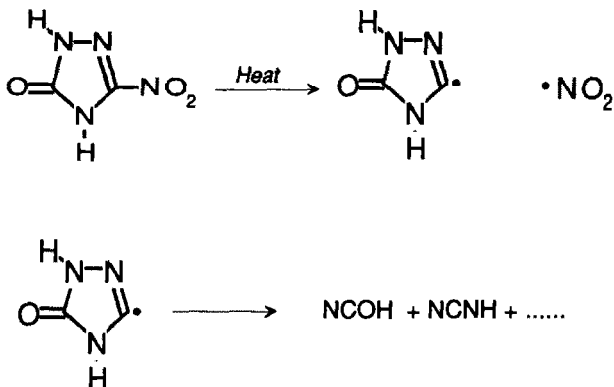
Fig. 5. Thermal decomposition path for NTO.

Lowering the laser pulse power gives us less thermal decomposition, and decreasing the EI voltage (or using chemical ionisation) gives us a way of distinguishing between the thermal fragmentation and fragmentation caused by the mass spectrometer. The LI-MS method produces a lot of data and only a small amount of this can be presented here. A summary of the measurements can be found in Table 1, which shows the most important "thermal" fragments in the decomposition zone and the probable (possible) assignments of these. In the column called strength, a relative measurement of peak abundance is used, where 1 denotes the most intense peaks and 4 denotes the weakest. Some distinct properties can be found in these spectra: (1) the presence of a relatively large amount of NO$_2$ (m/z 46) in the decomposition zone, the relative amount of NO$_2$ increasing with decreasing laser power; and (2) the existence of at least three peak groups (two large and one small) where the large peak groups mainly consist of masses with m/z 41–44 (azole ring breakdown components). The results of these measurements indicate that the first two steps in the thermal decomposition chain of NTO is an elimination of a NO$_2$ group (possibly in conjunction with the elimination of a hydrogen atom or a concerted elimination of HONO) followed by a breakdown of the azole ring. This proposed decomposition path is shown in Fig. 5. The similarities of the LI-MS spectra to the normal mass spectrum discussed earlier further strengthen this conclusion.

Chemiluminescence and DSC

The basic thermal stability of NTO was measured by DSC. Runs were carried out using a Mettler 800 with a heating rate of 0.1°C min^{-1} in the range 25–350°C. The DSC spectra showed only one peak, a very strong exothermic peak at 253°C. The peak is very distinct but has a slight shoulder. An extrapolated onset temperature of 270°C has been reported

in ref. 8. This paper also states that a broad shoulder occurs during the runs. We saw this type of behaviour when we used higher heating rates, for example 10°C min^{-1}.

The thermal stability of NTO was also studied by a chemiluminescence method [9, 19] (only NO detection). The CL method has earlier been used for decomposition studies at low temperatures [20, 21]. These studies indicated that the CL method is useful for determining the kinetic parameters of a high explosive at low temperatures. Equipment using the chemiluminescence reaction between nitric oxide and ozone has been built. It is primarily used for studying NO development from explosives at different temperatures. The high sensitivity of the NO analysis makes determination of NO production from propellants (e.g. nitrocellulose propellants) possible during short periods (minutes) even at room temperature. A description of the chemiluminescence apparatus can be found in ref. 19. This method was developed for the analysis of propellants and is not yet fully tested on high explosives. Because of this, not only were the activation energy and the frequency factor for NTO measured, but a comparison with RDX and TNT was also made; see Fig. 6. In this figure the production rate of NO is shown as a function of the temperature for NTO, RDX, and TNT. Assuming zero order Arrhenius kinetics, one can estimate the frequency factor and activation energy. Figure 7 is an Arrhenius plot for NTO, showing the mean values of four
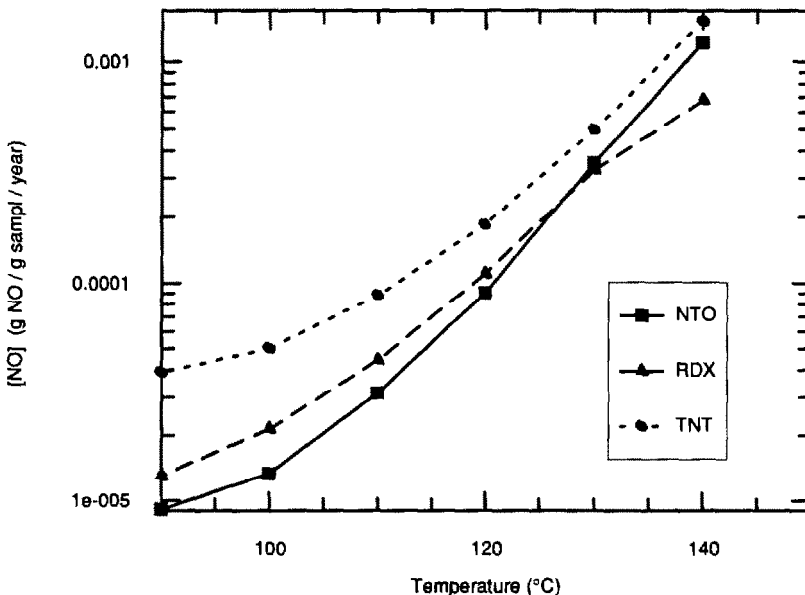

Fig. 6. The NO production rate of NTO, RDX and TNT measured by chemiluminescence.
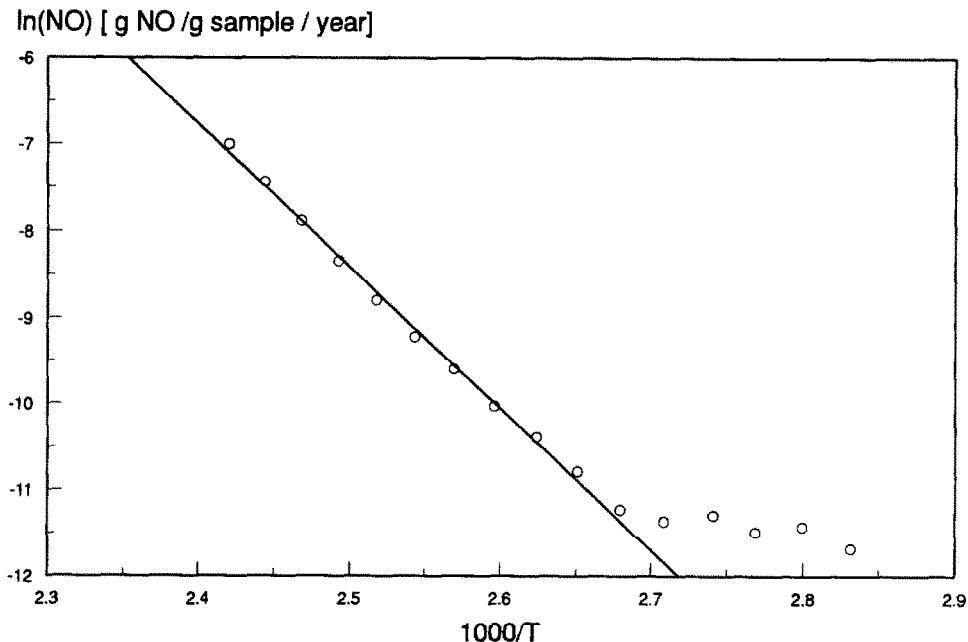
ln(NO) [g NO /g sample / year]

Fig. 7. Arrhenius plot for NTO (1000/T vs. ln[NO]).

runs, two with increasing and two with decreasing temperatures. From these measurements we calculated the activation energy as 140 kJ mol^{-1} and the frequency factor as 5×10^6 s^{-1} (for a temperature interval of 100–140°C). For lower temperatures the NO background was too large for any accurate measurements. These measurements clearly show the high thermal stability of NTO at low temperatures. The validation for using only NO as a measurement for the decomposition can be found in refs. 20 and 21.

QM CALCULATIONS

In order to explain the high stability of NTO and verify the initial step in the decomposition path, some-empirical, QM calculations were performed. We began our calculation by looking at the NTO C–NO$_2$ unimolecular bond scission [22]. The results, which are shown in Fig. 8, were computed with the MOPAC 6.0 code using the semi-empirical modified neglect of diatomic overlap (MNDO) [23] method with the parametric method 3 (PM3) [24] parameter set at the unrestricted Hartree–Fock (UHF) level. The potential energy surface for the uni-molecular bond scission of NTO (C–NO$_2$ bond) was generated by fixing the C–N bond and then fully optimising the geometry in a number of steps around the equilibrium value. The bond scission energy, ΔE^*, was found to be 255 kJ mol^{-1}. The same calculations were performed for the two
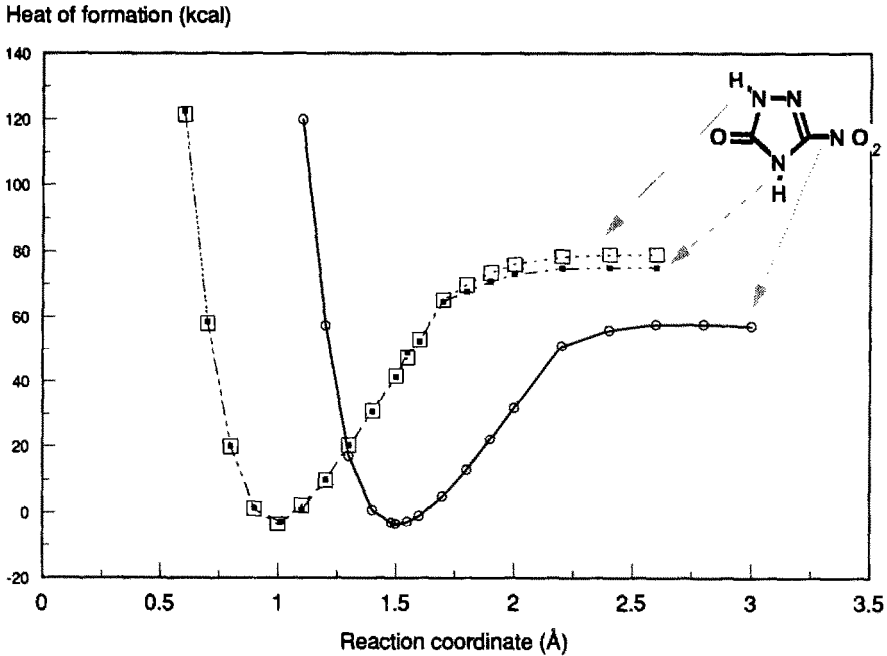
Heat of formation (kcal)

Fig. 8. Potential energy surface for the unimolecular bond scissions of NTO (N–H, C–NO₂).

N–H bonds. The ΔE^* for these bonds was 328 and 345 kJ mol⁻¹, respectively. These calculations verify that the weak bond in NTO is the nitro C–N bond and not the N–H bond. Using semi-empirical methods for calculating absolute heat of reaction or heat of formation in a reaction involving either bond breaking or bond formation normally gives questionable results. However, when one is interested only in comparing different reaction channels, reasonable results may be obtained [25]. We shall try to verify these results through ab initio quantum mechanical calculations. In these studies the geometry of the transition state will also be calculated.

CONCLUSIONS

The following conclusions can be drawn from the measurements and the QM calculations presented in this paper.
(1) The molecular sensitivity of NTO is far less than that of RDX and TNT.
(2) The thermal sensitivity is comparable with that of TNT.
(3) The probable thermal decomposition mechanism is an elimination of NO₂ followed by a breakdown of the azole ring.
(4) Semi-empirical QM calculation (MNDO method with the PM3 parameter set at the UHF level) verifies that the weak part of the NTO molecule is the C–NO₂ bond and not any of the N–H bonds.

REFERENCES

1 K.Y. Lee, L.B. Chapman and M.D. Coburn, J. Energ. Mater., 2 (1987) 27.
2 A. Becuwe, Utilisation du 5-oxo, 3-nitro,1,2,4-triazole comme substance explosiv et composition pyrotechnique contenant du 5-oxo,3-nitro,1,2,4-triazole, French Patent, No. 2584006 A1, 28 June 1985.
3 J.S. Boyer, Nitroazoles: The *C*-Nitro Derivatives of Five Membered N- and N,O-Heterocycles, Organic Nitro Chemistry Series, Vol. 1, VCH Publishers, Deerfield Beach, FL, 1986.
4 J.P. Ritchie and E.M. Kober, Proc. 9th Int. Symp. on Detonation, Vol. II, OCNR 113291-7, Portland, OR, 1989, pp. 1185–1192.
5 J.P. Ritchie, J. Org. Chem., 54 (1989) 3553.
6 J.P. Ritchie, K.-Y. Lee, D.T. Cromer, E.M. Kober and D.D. Lee, J. Org. Chem., 55 (1990) 1994.
7 A. Langlet, 3-Nitro-1,2,4-triazol-5-one (NTO): Ett nytt sprängämne med hög prestanda och låg känslighet, National Defence Research Establishment, FOA Rep. C 20789-2.3, March 1990.
8 E.F. Rothgery, D.E. Audette, R.C. Wedlich and D.A. Csejka, Thermochim. Acta, 185 (1991) 235.
9 H. Östmark, H. Bergman, G. Åqvist, A. Langlet and B. Persson, 16th Int. Pyrotechnics Seminar, Jönköping, Sweden, June 24–28 1991, p. 874.
10 G.J. Chipen, R.P. Bokalder and V.Ya. Grinshtein, Khim. Geterotsikl. Soedin., 2 (1966) 110.
11 J. Stals, Trans. Faraday Soc., 6 (1971) 67.
12 A. Alm, O. Dalman, I. Frölén-Lindgren, F. Hultén, T. Karlsson and M. Kowalska, Analyses of Explosives. Physical-chemical data, chromatograms, mass-, IR- and NMR-spectra. Colour reactions and thin layer chromatography, National Defence Research Establishment, FOA Rep. C 20276–D1, October 1978.
13 A. Pettersson, LIF och emissionsspektroskopi för studier av explosivämmen, National Defence Research Establishment, FOA Rep. D 20184-2.3, January 1992.
14 H. Östmark and R. Gräns, J. Energ. Mater., 8 (1990) 308.
15 H. Östmark, H. Nilsson, Proc. 9th Int. Symp. on Detonation, Vol. 1, OCNR 113291-7, Portland, OR, 1989, p. 65.
16 H. Östmark, H. Bergman, Fast laser pyrolysis of explosives combined with mass spectral study of the ignition zone, to be published.
17 R. Behrens Jr., Rev. Sci. Instrum., 58 (1986) 451.
18 X. Zhao, E.J. Hintsa and Y.T. Lee, J. Chem. Phys., 88 (1988) 801.
19 S. Berglund, National Defence Research Establishment, Rep., in preparation.
20 N.H. Volltrauer and A. Fontijn, Combust. Flame, 41 (1981) 313.
21 D.B. Olson and R.J. Gill, in Preprints of the Symposium on Compatibility of Plastics and Other Materials with Explosives, Propellants, Pyrotechnics & Processing of Explosives, Propellants and Ingredients, Head Island, SC, 1985, p. 96.
22 P.J. Haskins and M.D. Cook, Proc. 8th Int. Symp. on Detonation, NSWC MP 86-194, Albuquerque, NM, 1985, p. 827.
23 M.J.S. Dewar and D.M. Storch, J. Am. Chem. Soc., 99 (1977) 4899.
24 J.J.P. Stewart, J. Comput. Chem., 10 (1989) 209.
25 Y. Shi and S.M. Senkan, J. Phys. Chem., 95 (1991) 518.