

**THERMAL DECOMPOSITION OF Li(NTO)·2H₂O AND Na(NTO)·H₂O
(NTO = ANION OF 3-NITRO-1,2,4-TRIAZOL-5-ONE):
KINETICS DERIVED FROM T-JUMP/FTIR SPECTROSCOPY**

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A "snapshot" simulation of the surface reaction zone is captured by a thin film of material heated rapidly to temperatures characteristic of the burning surface by using the T-jump/FTIR spectroscopy. The time-to-exotherm (t_x) kinetics method derived from the control voltage trace of the Pt filament can be introduced to resolve the kinetics of an energetic material owing to its high sensitivity to the thermochemical reactions. The kinetic parameters of the two title compounds are determined under different pressures. The results show that Li(NTO)·2H₂O and Na(NTO)·H₂O (NTO = anion of 3-nitro-1,2,4-triazol-5-one) exhibit weak pressure dependence, their decomposition is dominated by the condensed phase chemistry irrespective of the pressure in the 0.1–1.1 MPa range. The values of E_a determined here are smaller than those given by a traditional non-isothermal differential scanning calorimetry (DSC) method, which might be resembled as the surface of explosion more closely and enabled the pyrolysis surface to be incorporated into models of steady and possibly unsteady combustion. The kinetics can also be successfully used to understand the behavior of the energetic material in practical combustion problems.

Keywords: Lithium; Sodium; Triazoles; 3-Nitrotriazolonates; Kinetics; Decomposition; T-jump/FTIR spectroscopy; Flash pyrolysis; Explosives.

3-Nitro-1,2,4-triazol-5-one (NTO, Chart 1 has recently emerged as a potential high performance insensitive explosive with performance properties comparable to that of RDX and sensitivity close to that of TATB^{1–6}. NTO easily forms salts with many metal ions^{7–9} owing to its acidic nature ($pK_a = 3.67$)¹. Brill et al.¹⁰ have shown that metal salts of NTO form volatile metal compounds during thermolysis, which may be further converted to metal oxides in the gas phase. They have suggested the addition of some metal salts so as to dampen high-frequency acoustic modes inside the combustor and, thus, to avoid unsteady combustion. Singh et al.^{9,11–13} has evaluated

the activity of some of these salts in HTPB-AP and HTPB-AN composite solid propellants. Metal salts of NTO are reported as potential primary explosives as well as ballistic modifiers. They are assumed to achieve a catalytic effect on burning rate without much adverse effect on the energetics of the propellants.

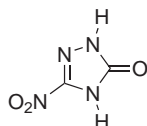


CHART 1
Chemical structure of NTO

Kinetic parameters of energetic materials are of great importance for understanding such processes as ignition, combustion and explosion. Explosive properties and non-isothermal mechanisms of thermal decomposition of NTO salts have been studied using DSC, TG-DTG and FTIR methods¹⁴, the kinetics are determined by the Kissinger method, Ozawa method and others. However, the kinetics determined by DSC method is not applicable to the combustion conditions owing to the relatively low heating rates. Consequently, the T-jump/FTIR¹⁵ spectroscopy is introduced to detect gas products of flash pyrolysis and to measure the kinetics of the exothermic decomposition under the conditions more closely resembling the surface of the explosive during explosion.

The time-to-exotherm (t_x) values derived from the control voltage traces of the Pt filament can be used in conjunction with the theory of thermal explosion to determine the overall kinetics, this method has recently been applied to several energetic materials¹⁶⁻¹⁸. The aim of this work is to study the kinetics of flash pyrolysis of $\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$ and $\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$. These data are quite useful in the evaluation of thermal stability and can be incorporated into models of steady and possibly unsteady combustion.

EXPERIMENTAL

Sample Preparation

The lithium and sodium salts of NTO were synthesized by neutralization of NTO with the corresponding hydroxides^{7,8}. The obtained crystals were washed with distilled water, dried in vacuum at 60 °C for 6 h; They had the following compositions: $\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$ and $\text{Na}(\text{NTO}) \cdot \text{H}_2\text{O}$.

T-jump/FTIR Spectroscopy

The flash pyrolysis of the title compounds was conducted by using the T-jump/FTIR spectroscopy¹⁵. The IR cell¹⁹ consisted of two antireflection-coated ZnSe windows and a 3.8 cm path length. The Pt filament was situated along the axis of the IR cell about 3 mm below the focal point of the IR beam. Briefly, approximately 300 µg of a sample was spread on the center of the Pt filament. The filament was inserted into the spectroscopy cell and connected to the CDS Analytical. The cell was then flushed with Ar gas and the required pressure was adjusted. Pressures of 0.1–1.1 MPa were used. The filament temperature was calibrated under each pressure using the compounds with standard melting points. The power supply was set to heat the filament to ca. 2000 °C s⁻¹, but heat transfer effects limited the heating rate of the sample to ca. 800 °C s⁻¹ (refs.^{20,21}).

The Pt filament was an element of a very rapidly responding and sensitive circuit²². The difference control voltage trace (sample trace minus reference trace) for the Pt filament qualitatively indicated the sequential thermochemical events of the compound. An endotherm such as melting or release of hydration H₂O produced an upward deflection, whereas a downward deflection marked an exotherm, such as decomposition of the energetic component. Under idealized conditions the trace profile could be used quantitatively²³, but normally it was better to use it merely as qualitative detection of thermochemical changes.

The spectra of the gas products were recorded simultaneously with the measurement of the control voltage of the Pt filament. The complete IR spectrum of the thermally quenched gas products was collected in 0.25-s intervals with 4 cm⁻¹ resolution on a Nicolet 20SXB FTIR spectrometer with an MCT detector. The relative concentrations of the gas products were obtained by a procedure employing the effective width factors and absolute intensities of non-interfering absorbances for each product^{19,24,25}. CO₂ was the standard for determining the relative concentration of all other gases. The theoretical basis for the procedure was based on the Lambert–Beer law. The gas products from Li(NTO)·2H₂O and Na(NTO)·H₂O were quantified¹⁰, which showed the salt produced a volatile metal isocyanate upon flash pyrolysis.

Determination of the Kinetics of the Exothermic Decomposition Reaction

An exotherm produces a sharp spike in the control voltage trace, which marks the time-to-exotherm value. The value can not only be employed to outline the chemistry that takes place within the simulated surface reaction zone, but also can determine the kinetics of the flash pyrolysis of the compound.

$$\ln(1 - \alpha) = k(T)t \quad (1)$$

The first-order rate expression is shown in Eq. (1), where α is the amount of sample decomposed at time t , whose relationship to $k(T)$ for a first-order process is given by the heat balance Eq. (2). Wherein λ is the thermal diffusivity, C_p is the specific heat capacity, Q is the heat of reaction, which can be derived from the DSC measurement.

$$-\lambda \nabla^2 T + \rho C_p (dT/dt) = \rho Q A (1 - \alpha) e^{-E_a/RT} \quad (2)$$

It is well known that $\lambda \nabla^2 T = 0$ under adiabatic conditions^{26,27}. The time-to-exotherm is equivalent to the time-to-explosion analyzed by Semenov for a thermal process^{28,29}. Equa-

tion (3) can be used to determine apparent Arrhenius-like kinetic parameters, where t_x is the time-to-exotherm value at temperature T .

$$\ln t_x = E_a/RT + \gamma \quad (3)$$

The intercept, γ , is not the conventional Arrhenius pre-exponential factor A , but is assumed to be about $-\ln A$ (ref.¹⁶). The values of E_a and γ are chosen to give the overall decomposition rate. They do not refer to a specific reaction or event.

The difference control voltage traces of the Pt filament under 0.1 and 1.1 MPa of argon are shown in Fig. 1, from which we can get the time-to-exotherm (t_x) values of the flash pyrolysis of $\text{Li}(\text{NTO})\cdot 2\text{H}_2\text{O}$ in the 328–348 °C range. The temperature range chosen lies 60–100 °C above the decomposition temperature measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The experimental measurements of t_x

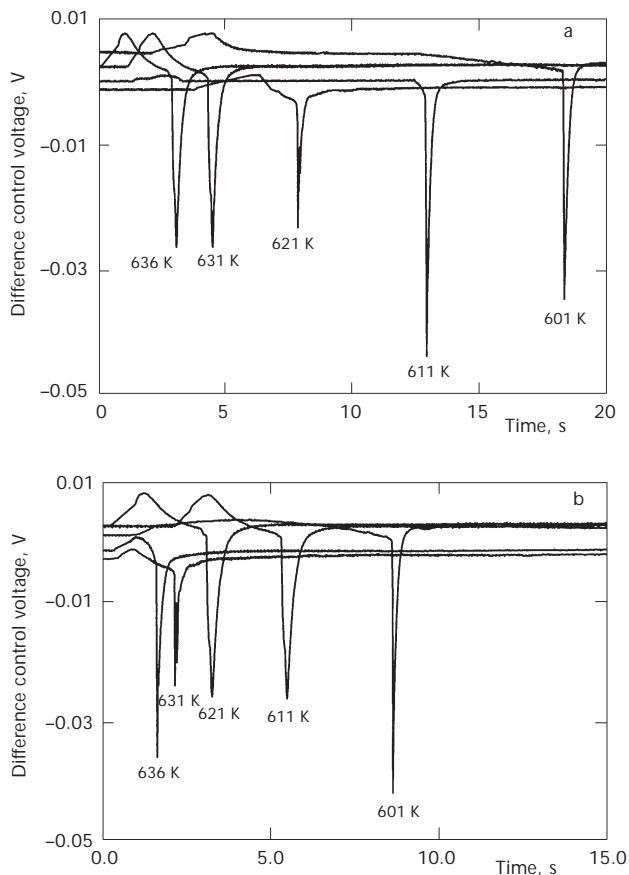


FIG. 1
The difference control voltage traces of the Pt filament of $\text{Li}(\text{NTO})\cdot 2\text{H}_2\text{O}$ at 0.1 MPa (a) and 1.1 MPa (b) of Ar

are then plotted vs $1/T$ (shown in Fig. 2) to obtain the activation energy E_a and $\ln A$. This yields $E_a = 164.28 \text{ kJ mol}^{-1}$, $\ln A = 29.84$ at 0.1 MPa and $E_a = 158.18 \text{ kJ mol}^{-1}$, $\ln A = 29.46$ at 1.1 MPa.

Similarly we get the time-to-exotherm (t_x) values of $\text{Na}(\text{NTO})\cdot \text{H}_2\text{O}$ at 0.1 and 1.1 MPa in the 311–361 °C range from the control voltage traces of the Pt filament. The kinetic parameters are determined from the Arrhenius-plot (shown in Fig. 3): $E_a = 98.27 \text{ kJ mol}^{-1}$, $\ln A = 17.09$ at 0.1 MPa and $E_a = 98.23 \text{ kJ mol}^{-1}$, $\ln A = 18.11$ at 1.1 MPa.

RESULTS AND DISCUSSION

The external pressure applied to the compound that evolves gas products as a result of thermal decomposition can have a major impact on the overall

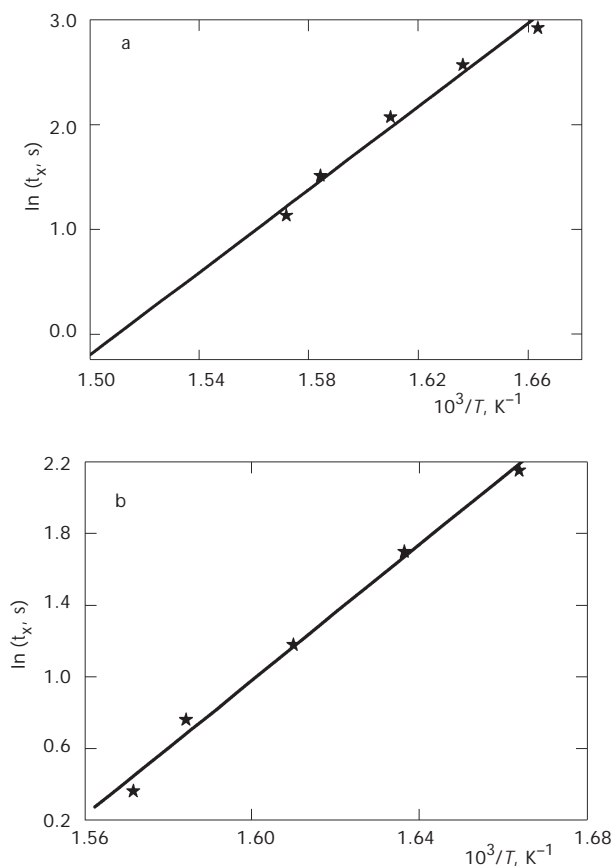


FIG. 2
The Arrhenius-type plot of the time-to-exotherm for $\text{Li}(\text{NTO})\cdot 2\text{H}_2\text{O}$ at 0.1 MPa (a) and 1.1 MPa (b) of Ar

process³⁰. The initially produced reactive gas products must percolate through the condensed phase before they reach the IR beam. Pressure influences the rate of diffusion and, thus, the time of percolation and thereby changes the extent of the reaction of these gases with the condensed phase. Increasingly stable gas products appear with increasing pressure because the time for that the reactive gases are in contact with the condensed phase is longer. The kinetics is approximately of the same value. It has been found that the gas products depend negligibly on the pressure in the tested pressure range (0.1–1.1 MPa)¹⁰. It can thus be concluded that $\text{Li}(\text{NTO})\cdot 2\text{H}_2\text{O}$ and $\text{Na}(\text{NTO})\cdot \text{H}_2\text{O}$ both among the compounds exhibiting weak pressure dependence.

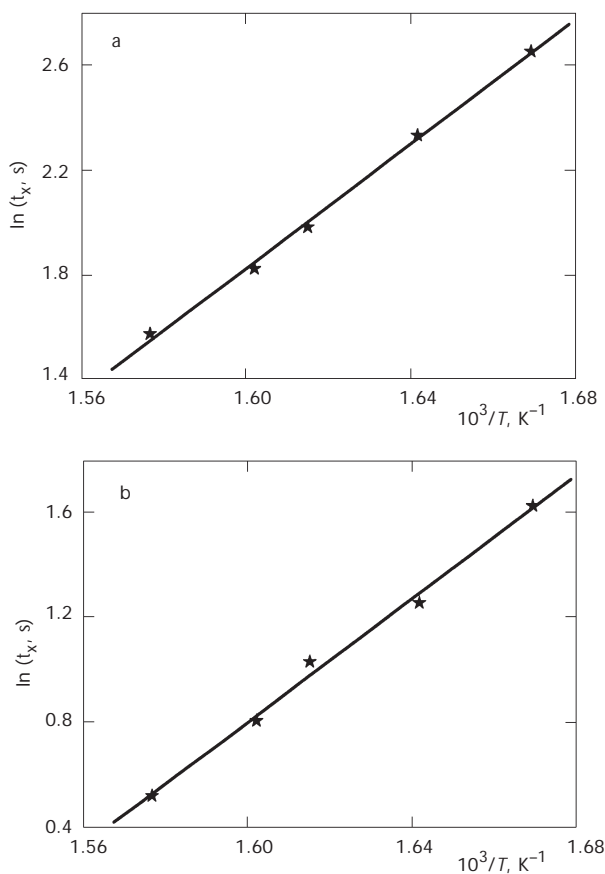


FIG. 3
The Arrhenius-type plot of the time-to-exotherm for $\text{Na}(\text{NTO})\cdot \text{H}_2\text{O}$ at 0.1 MPa (a) and 1.1 MPa (b) of Ar

The two compounds appear to have reacted to a considerable extent in the condensed phase before the gas products are detected. Reactive gas products probably form early but do not escape in high concentrations because of consecutive reactions with other products in the condensed phase. The decomposition of the two compounds is dominated by the condensed phase chemistry irrespective of pressure in the 0.1–1.1 MPa range. Another possible way is that it may involve competing, parallel, gas generating reactions leading to similar products. The extent of these reactions may shift with pressure and compensate one another.

The activation energy E_a of the exothermic decomposition reaction of Li(NTO)·2H₂O was determined to be 319.9 kJ mol⁻¹ by Kissinger method ($E_a = 313.1$ kJ mol⁻¹ by Ozawa–Doyle method), $\ln A = 63.99$ in the previous study¹⁴. The kinetic parameters of the exothermic decomposition reaction of Na(NTO)·H₂O was also determined: $E_a = 185.7$ kJ mol⁻¹ by the Kissinger method ($E_a = 185.0$ kJ mol⁻¹ by the Ozawa–Doyle method) and $\ln A = 37.16$.

The values determined here for the exothermic decomposition reaction of Li(NTO)·2H₂O and Na(NTO)·H₂O at 0.1 MPa by using the T-jump/FTIR spectroscopy are much smaller than those found previously by a traditional non-isothermal DSC method, the trend also occurs with other energetic materials such as HMX and RDX³¹.

A wide knowledge of Arrhenius parameters is usually necessary for heterogeneous reactions, the terms of “activation energy”, “pre-exponential factor” are retained but do not necessarily have the same meaning as in homogeneous-phase kinetics^{18,32}. Two apparent activation energies for surface processes must be distinguished. These are the surface activation energy and the chemical activation energy. The surface activation energy, E_s , is described by pyrolysis Eq. (4). The measured linear regression rates, r , at various surface temperatures, T_s , determine the value of E_s . The surface regression to which Eq. (4) applies is of zeroth order. The kinetics determined above is, in fact, the surface activation energy, E_s .

$$r = A_s e^{-E_s/RT_s} \quad (4)$$

Starting with Merzhanov and Dubovitskii³³, a number of authors^{34,35} have shown that $E_s < E_a$ for many propellants. The values of E_s are usually small compared with the strength of the weakest bond in energetic molecules and the overall Arrhenius parameters for decomposition of HMX and RDX³¹ derived from DSC, TGA and manometry, which makes the values determined herein qualitatively consistent. The kinetics determined in this work more in details resemble that of the surface of the explosive during

explosion, thus, it should enable the surface pyrolysis to be incorporated into models of steady and possibly unsteady combustion.

CONCLUSIONS

By simultaneously recording the control voltage and the rapid-scan IR spectra of the near surface gas products considerable details about the chemical mechanism relevant to combustion of an energetic material can be learned using the T-jump/FTIR spectroscopy. It can also be introduced to determine the kinetics of the exothermic decomposition reaction of the flash pyrolysis of the energetic material. The time-to-exotherm (t_x) obtained from the control voltage traces of the Pt filament yields the kinetics of Li(NTO)·2H₂O in the 328–348 °C range under 0.1 MPa argon atmosphere: $E_a = 164.28$ kJ mol⁻¹, $\ln A = 29.84$. For Na(NTO)·H₂O $E_a = 98.27$ kJ mol⁻¹, $\ln A = 17.09$ in the 311–361 °C range under 0.1 MPa argon atmosphere.

The results show that the two compounds exhibit weak pressure dependence. Its decomposition is dominated by the condensed phase chemistry irrespective of the pressure in the 0.1–1.1 MPa range. Another possibility is that it may involve competitive, parallel, gas-generating reactions leading to similar products. The extent of these reactions may shift with pressure and compensate one another.

However, a major difference exists between traditional non-isothermal DSC method and the T-jump/FTIR spectroscopy, which also occurs with other energetic materials making these values qualitatively consistent. The kinetics measured by T-jump/FTIR spectroscopy might be resembled as the surface of explosion more closely and used profitably to understand the behavior of the energetic material in practical combustion problems. The kinetics determined can also enable the pyrolysis surface to be incorporated into models of steady and possibly unsteady combustion.

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