

Energetic Materials of the Nitropyrazole Family: Unusual Thermal and Combustion Behaviors

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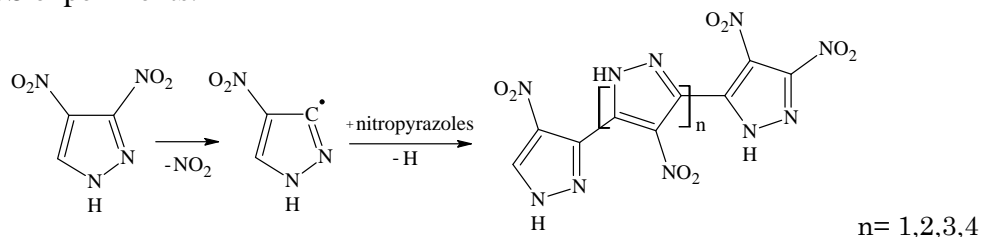
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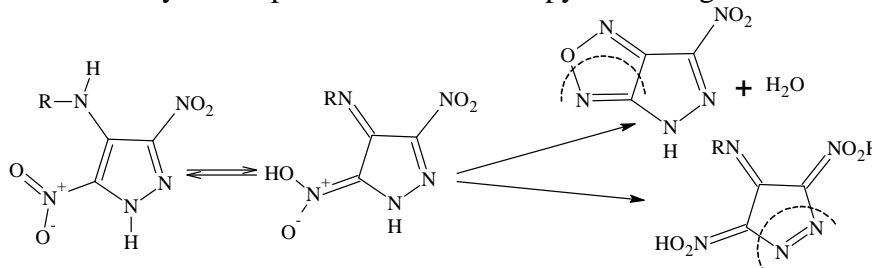
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Despite intensive recent activities in studying the thermal behavior of the nitropyrazoles, the decomposition kinetics and mechanism still raise many questions. Besides, no experimental data on combustion behavior of the nitropyrazoles have been available in the literature by the beginning of our research. The purpose of the present work was to investigate thermal decomposition and burning behaviors of several compounds of the nitropyrazole family. The following nitropyrazoles were selected as objects for the study: (i) compounds containing two nitro groups - 3,4-dinitro-1H-pyrazole (3,4-DNP) and its bicyclic analog 3,3',4,4'-tetranitro-1,1'H-bipyrazole-5,5' (TNBP); 4-amino-3,5-dinitro-1H-pyrazole (ADNP) and its substituted analog N-(3,5-dinitro-1H-pyrazol-4-yl)-[1,2,4]triazolo[4,3-b][1,2,4,5]tetrazin-6-amine (ADNPTrTz); (ii) compounds containing three nitro groups - 3,4,5-trinitro-1H-pyrazole (TNP) and 1-methyl-3,4,5-trinitro-1H-pyrazole (MTNP).

The decomposition of dinitropyrazoles, 3,4-DNP and TNBP, begins with a loss of the nitro group. The pyrazole moiety is resistant to oxidation by NO₂, which leads to a low heat effect at the initial decomposition stage and brings about some difficulties in deriving real kinetics from DCS experiments.



The decomposition of mononitro substituted oligomeric pyrazoles occurs in the second stage at temperatures above 300 °C. The activation energies of the cleavage of the first and last nitro group differ insignificantly (38.5-38.9 and 41.1-43.7 kcal/mol), while the rate constants differ by almost 2 orders of magnitude (Fig.1 and Fig.2). If the nitropyrazole molecule contains the amino group, the thermal decomposition may begin with NO₂ group isomerization followed by decomposition of either the pyrazole ring or formed furazan cycle.



In the latter case, the activation energy of decomposition appeared to be rather low (26 kcal/mol for ADNP) (Fig.3) that might be indicative of low thermal stability of nitropyrazole. The stability of the trinitroderivatives differs insignificantly (Fig.3), which excludes decomposition through the aci-form of the NO₂-group assumed earlier in some papers. The rate constants of the initial stage of TNP and MTNP decomposition are close to the decomposition rate of 3,4-DNP, which indicates the same initial stages. However, in contrast

to 3,4-DNP, gaseous decomposition products of TNP and MTNP do not contain NO_2 and the decomposition proceeds through destruction of the pyrazole ring.

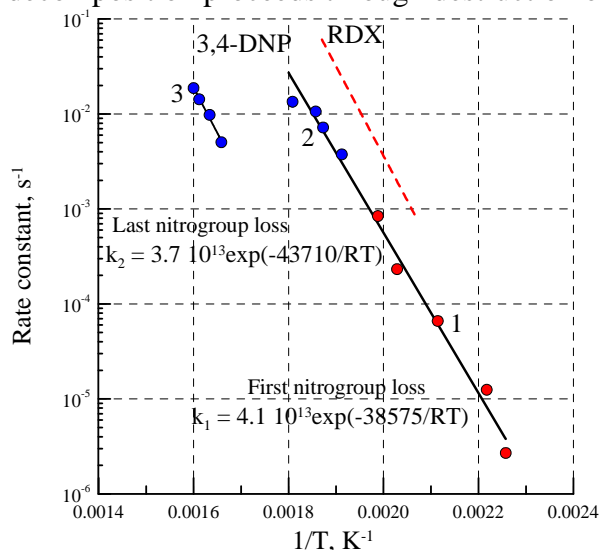


Fig. 1. A comparison of rate constants of RDX decomposition and rate constants of the first (1,2) and the last (3) nitrogroup detachment in 3,4-DNP, obtained in isothermal (1) and non isothermal (2, 3) conditions.

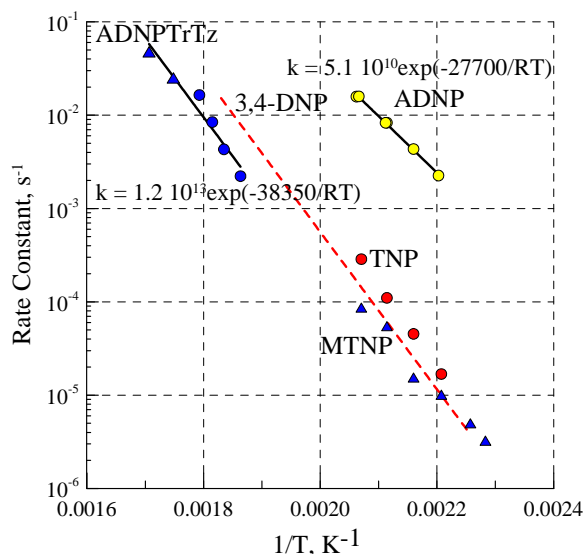


Fig. 3. A comparison of decomposition rate constants for 3,4-DNP, ADNP, ADNPTTrTz, TNP and MTNP in the liquid state.

Nitropyrazoles demonstrate a wide range of combustion rates (Fig.4). Thermocouple studies of the combustion wave of nitropyrazoles have shown that their burning rates are determined by the kinetics of reactions in the melt at the surface temperature that is controlled by evaporation. Differences in the burning rates of nitropyrazoles with a similar decomposition kinetics are explained by differences in surface temperatures. A shortage of heat to warm up the compound to the surface temperature is supposed to be a reason for (a) the observed combustion instability of ADNP and ADNPTTrTz at low pressures, (b) high pressure limit of 3,4-DNP combustion, and (c) inability of TNBP to burn at pressures up to 20 MPa.

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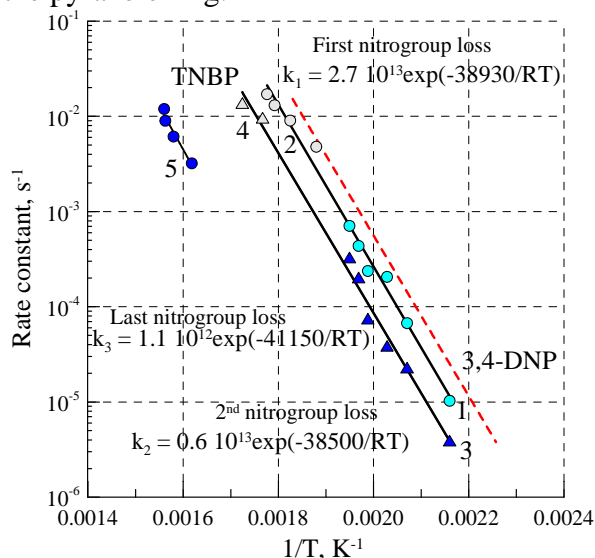


Fig. 2. A comparison of rate constants for 3,4-DNP decomposition, the first nitrogroup detachment from each circle (1,2 and 3,4) and the last nitrogroup detachment (5) in TNBP, obtained in isothermal (1,3) and non isothermal (2,4,5) conditions.

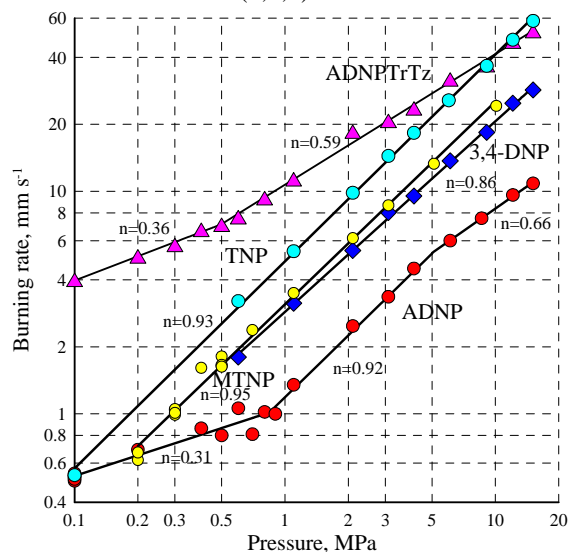


Fig. 4. A comparison of burning rate vs. pressure dependencies for ADNP, 3,4-DNP, ADNPTTrTz, TNP and MTNP.