THEORETICAL EVALUATION OF THE CHANGE IN DETONATION CHARACTERISTICS OF ENERGETIC AMINES UPON CONVERSION INTO TRIAZENES AND PENTAZOLES

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Aromatic and heterocyclic amines form a huge pool of modern energetic materials, both molecular and salt-like [1]. Simultaneous presence of amino and notro groups in an energetic molecule provide benefit in stability due to strong intramolecular hydrogen bonds, like in 1,3-diamino-2,4,6-trinitrobenzene (DATB) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), which results in high h_{50} values equal 320 and 490 cm, respectively [2]. Additionally, such amines can be converted into diazoaminoarenes (triazenes) and pentazoles via formation of diazolium salt as an intermediate (Fig. 1) [3]:

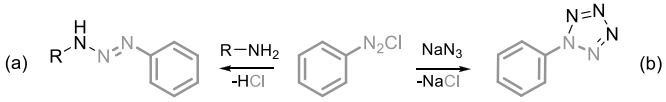

Fig. 1. Schematic presentation of the reactions studied in this work

According to our recently proposed method [4], these reactions can be schematically illustrated as the following (left – triazene, right – pentazole):

$$C_{2x}H_{2y-3}N_{2z+1}O_{2w} \leftarrow \mathbf{C_xH_yN_zO_w} \rightarrow C_xH_{y-2}N_{z+4}O_w \qquad (1)$$

As a result, one can expect the following increase in density and heat of formation (Table 1).

Table 1. General expression for gain in density (Δd_c) and heat of formation ($\Delta\Delta H_f$)

Route	Δd_c	$\Delta\Delta H_f$
(a)	$\frac{1.020(a_1x+b_1y+c_1z+w)}{(a_2x+b_2y+c_2z+w)(a_2x+b_2y+c_2z+w-0.091)}$	–1.2845(–32x + 26y – 89z + 56w – 167)
(b)	$\frac{2.398(a_3x+b_3y+c_3z-w)}{(a_2x+b_2y+c_2z+w)(a_2x+b_2y+c_2z+w+4.386)}$	1.2845(4N – 2H) = 524.1 kJ mol^{-1}

Herein, a_1 = 1.457, b_1 = 0.418, c_1 = 1.255, a_2 = 1.643, b_2 = 0.512, c_2 = 1.355, a_3 = 2.201, b_3 = 1.423 and c_3 = 0.712. Thus, one can easily calculate how much the detonation characteristics will increase for an arbitrary composition $C_xH_yN_zO_w$, which corresponds to an aromatic or heterocyclic amine. This is a convenient method for a crude estimation of the detonation properties without any quantum-chemical calculations. Of course, the latter are still needed for a precise estimation, but now these expensive methods can be applied for a much shortened list of potential candidates.

References

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