HNF FLAME – ALTERNATIVE MECHANISM OF GAS FLAME REACTIONS

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Hydrazine nitroformate ($N_2H_5C(NO_2)_3$ – HNF) is a product of reaction between hydrazine N_2H_4 and trinitromethane $HC(NO_2)_3$ (nitroform – NF). The HNF is considered as a promising candidate for substitution of ammonium perchlorate when designing high energy solid propellants with ecologically friendly combustion products. Detailed study of the physicochemical properties and decomposition and combustion mechanisms of HNF started rather recently [1-6] and available information is restricted. Therefore the development of comprehensive models of HNF decomposition/combustion is faced with essential difficulties and all current accomplishments have to be treated as preliminary ones. Below briefly we discuss the combustion mechanism of HNF proposed in [3] and formulate an alternative mechanism for gas phase reactions in the flame of HNF, which was tested via comparison with experimental data on temperature and species concentration profiles known from literature.

Experimental data on decomposition and combustion of HNF

Thermal decomposition of HNF in the liquid phase was studied in [7] with use of the T_{jump}/FTIR spectroscopy approach. The study was conducted in the temperature range 130-400^{0}C at pressures of 5-7 atm. The melting point of the HNF investigated was equal to 123^{0}C. Under heating up to 130-260^{0}C, the species of $HC(NO_2)_3$, N_2H_4, N_2, H2O, CO and aerosol particles of ANF (ammonium nitroformate) were detected in the gas phase. According to Ref. 7 the formation of above products occurs mainly in the condensed phase. Aerosol particles of HNF were not detected. The presence in the gas phase of N_2H_4 and NF testifies to dissociative evaporation by the route

$$HNF_{liq} \rightarrow NF_g + N_2H_{4\,g}$$

Data of temperature profile measurements in the combustion wave of HNF are presented in [4-6]. The W/Re ribbon thermocouples of 7-20μ thickness were used in the pressure range of 0.04-2.0 MPa. The density of pressed HNF samples was equal to 1.74-1.76 g/cm^3 (about 94% of TMD). According to experimental data [5], at low pressures several characteristic zones can be recognised in the combustion wave. The first zone corresponds to the heating of HNF from the initial to the melting temperature, T_m = 396-399K. The second zone is located in the melted layer, where the temperature gradually increases. For example, at P = 0.1 MPa temperature rises from 425K to 615K at the distance ~ 0.15 mm. The gas flame consists of two zones. In the first zone the temperature rises from T_s to 1320-1540 K depending on the pressure level. Then, after a relatively slow increase, the temperature sharply rises and reaches the level of 2300-2720 K, which is lower than the adiabatic flame temperature by 140-390 K at given pressures.

The thermocouple readings testified the noticeable rate of heat generation by the condensed phase reactions. In particular, the heat feedback from the gas phase at P=0.1 MPa is not sufficient for compensating the heat losses for the condensed phase heating up to the burning surface temperature [4]. When discussing the HNF combustion mechanism [4], it was proposed to take into account the dissociative evaporation of HNF from the burning surface.

The chemical structure of the HNF flame has been experimentally studied at atmospheric pressure in [1,2]. Maxima of curves for NH_2*, NH and CN profiles are located on the distance from the burning surface ~180, 300 and 360μ, respectively. The mole fraction of OH first grows sharply close to surface and increases gradually further in the flame reaching value of 0.024 at the distance of 4 mm from the surface.

The data [2] in the form of the Raman signal peak for N_2 were used for calculation of T(x) in the chosen points in the HNF flame, P=1 atm. It was found T=1800K at x=0.35 mm and 2766K at x=1.2 mm.

Comparison of these data with those reported in other sources reveals significant scatter in the temperature values (see Table 1).

Table 1

X, mm	0.35	1.2	4.0	Reference
T, K	1800	2766		2
T, K		~2100	~2300	8
T, K			~2700	3
T, K	~2650			4

Detailed combustion mechanism by Louwers

The combustion model based on detailed mechanism of chemical reactions in flame is formulated by Louwers [3] within the framework of one-dimensional isobaric approach. The gas phase reaction scheme consists of 204 elementary reactions involving 39 species. It is mainly based on the Yetter mechanism for RDX combustion [9] corrected by introduction of gaseous HNF decomposition steps. In addition, 3 global reactions for the gas phase decomposition of HNF vapor molecules were included.

For closing the system of equation a relationship is suggested that links the mass burning rate with the burning surface temperature T_s. This temperature is assumed to be equal to the HNF boiling temperature calculated from an additional equation. Decomposition of HNF in the liquid phase is described by 3 global reactions.

According to [3], simultaneously with decomposition the evaporation of HNF occurs in the liquid subsurface layer: $HNF_{liq} \rightarrow HNF_{vap}$. Decomposition of evaporated molecules of HNF in the gas phase is described by 2 global reactions: $2HNF = 4NO + 2CO + 4H_2O$

$+ 2N_2O + N_2 + H_2$

$2HNF = 4NO + 2CO_2 + 4H_2O + 3N_2 + H_2$

The first global reaction corresponds to the low temperature while the second one refers to the high temperature decomposition reactions of HNF molecule.

Alternative approach in modeling chemical processes in the flame of HNF

According to the calculations made by Louwers [3] more than 90% of HNF is evaporated from the burning surface. On the contrary, the alternative approach assumes that an essential part of HNF is decomposed in the liquid subsurface layer. It has been shown in numerous experimental studies that for the most of contemporary energetic materials exothermic reactions in the condensed phase play essential role. Similar findings were also made for HNF [5,10]. Unfortunately, these data are very restricted. Therefore, it is useful to analyze the experimental data [3] on sublimation of HNF in the temperature range (34.4 – 67.7)^{0}C. When measuring the equilibrium vapor pressure, it was established correlation in the form

$$P_{eq} \sim \text{const} \cdot \exp(-C/RT), \qquad (1)$$

where C = 530 J/g ≈ 23190 cal/mol. According to [3], the value of C in the case of evaporation of pure HNF corresponds fairly well to the sum of melting and evaporation heats $H_m + H_{evap}$ = 161 J/g + 350 J/g = 511 J/g. However, it has to be stressed that the evaporation heat can be calculated very approximately (15-20% error, at least) and above estimation could not serve as a reliable evidence of pure HNF evaporation.

Another option for HNF conversion on the crystal surface is presented by the dissociation reaction yielding 2 gas molecules:

$$HNF_s \rightarrow N_2H_{4\,g} + HC(NO_2)_{3\,g} \qquad (2)$$

In this case the equation (1) for the equilibrium pressure of gasification products takes the form:

$$P_{eq} \sim \text{const}\cdot\exp(-\Delta H/2RT) \qquad (3)$$

Here ΔH is the heat of reaction (Eq.2), which can be calculated with account of the temperature dependencies for specific heat of reactants with given values of ΔH^0_f (HNF), ΔH^0_f (NF), and $\Delta H^0_f(N_2H_4)$. The results of calculations are given in Table 2.

Table 2.

T, K	332	365
ΔH, kcal/mol	≈ 46,3	≈ 46,5

It follows from Table 2 the magnitude of ΔH/2 = 23150 ÷23250 cal/mol, which is close to the value of C = 23190 cal/mol reported in [3]. This result may serve as an indirect evidence of dissociative evaporation path for HNF. However, one may recognize that well substantiated choice of the evaporation scheme takes precise measurement of the vapor pressure and detection of the nature of gasification (evaporation) products.

Thus, in the present study we assume that on the burning surface of HNF the process of dissociative evaporation takes place in the form:

$$HNF_{liq} \rightarrow N_2H_{4\,g} + HC(NO_2)_{3\,g} \qquad (4)$$

As is stated in [11], simultaneously with the reaction (4) the HNF thermal decomposition in the liquid phase results in formation of ammonium nitroformate, $NH_4C(NO_2)_3$ that also may evaporate by the route:

$$NH_4C(NO_2)_{3\,liq} \rightarrow NH_{3\,g} + HC(NO_2)_{3g} \quad (5)$$

Totally, the burning surface generates a set of gaseous species resulted from dissociation reactions (4,5) as well as from thermal degradation reactions [7,11,12]. The correct knowledge of those species and their concentrations on the burning surface, which are used in the boundary conditions for solving the stationary combustion problem, is absent. Therefore, these data have to be first roughly estimated on the basis of available information and then matched in accordance with the conservation laws of energy and the number of elements.

In the present work, the detailed chemical reaction mechanism is described by 283 elementary steps based on 47 species, namely:

O, O2, H, H2, OH, H2O, HO2, N, N2, N2O, HNO, NH3, NH2, NO, NO2, N2H, NH, N2H2, H2O2, HNO2, HNO3, NO3, H2NO, N2H3, N2H4, CO, CO2, HCO, H2CO, CN, HCN, NHC, CNO, NCO, C2N2, HNCO, HOCN, HCNO, HC(NO2)3, HC(NO2)2, HCNO2, HC(O)NO2, C(NO2)2NOOH, C(NO2)NOOH, C(NO2)2NO, C(NO2)NO, HC(O)NO.

Excluding the elementary reaction $HC(NO_2)_3 \rightarrow HC(NO_2)_2 + NO_2$, the magnitudes of the reaction constants for the steps with participation of $HC(NO_2)_3$ and its fragments are not known. All calculations were performed under assumption that the control role belongs to the dissociation reaction of the NF molecule or its isomer dissociation:

$$HC(NO_2)_3 \rightarrow NO_2 + HC(NO_2)_2, \quad \text{or}$$

$$C(NO_2)_2NOOH \rightarrow NO_2 + C(NO_2)NOOH$$

The numerical calculations were performed using the technique described in [13]. In order to obtain data on the structure of the stationary gas flame of HNF at given pressure, the experimental value of the mass burning rate was used along with estimated values for the mole fraction of gas species and burning surface temperature. At the far distance from the burning surface the zero temperature and concentration gradient conditions were taken into consideration. For estimating the approximate values of fractions of gas species just above the burning surface the expressions for conservation laws of energy and elements without taking into account the thermal conductivity and diffusion processes were used. The number of acceptable data sets consisted of values of T and α_i, which fit the conservation equations, is extremely large. However, it can be diminished essentially if one takes into consideration experimental data on the temperature and species concentration profiles in the flame of HNF.

Below (Table 3) we present 2 sets of the molar fractions of the species chosen as the boundary condition on the burning surface for calculating the flame structure of HNF.

Table 3

set#	T_s	H_2O	N_2	N_2O
1	623	0.252	0.0259	0.155
2	620	0.180	0.0026	0.155
set#	T_s	NH_3	NO_2	NO
1	623	0.050	0.037	0.216
2	620	0.075	0.050	0.205
set#	T_s	HNO_2	N_2H_4	CO
1	623	0.012	0.050	0.050
2	620	0.050	0.075	0.062
set#	T_s	CO_2	H_2CO	HCN
1	623	0.025	0.0063	0.0015
2	620	0.050	0.0057	0.0054
set#	T_s	HCNO	NF	
1	623	0.067	0.050	
2	620	0.0333	0.050	

The values of specific enthalpy H and molar mass of the gas mixture for different data sets are the following: $H_1(T_s= 623\ K) = -100.26$ cal/g; $M_1 = 36.53$ g/mol; $H_2(T_s = 620\ K) = -100.84$ cal/g; $M_2 = 37.87$ g/mol.

It has to be mentioned that specific enthalpy for HNF at the temperature 298 K equals [14] $h^*/M^* = -100.2 \pm 1.4$ cal/g. This value corresponds fairly well to H_1 and H_2 magnitudes. The burning surface temperature values for listed sets agree within the experimental error with the data [4] at atmospheric pressure $T_s = 615 \pm 10$ K. The chosen sets of molar fractions of species in the gas phase just above the surface correspond to intense condensed phase exothermic reactions.

Preliminary, the calculations of the flame structure for model gas mixture N_2/NF were performed, which simulated the conditions of HNF combustion at P=1 atm. The calculations showed that the mixtures with $0.05 \leq \alpha_{NF} \leq 0.5$ exhibit self-sustaining flame driven by exothermic decomposition of NF. The temperature and species concentration profiles depend on the chosen scheme for the NF decomposition. This can be used for validation of the NF decomposition mechanism if conducting experiments with the N2/NF gas mixtures. Important finding is that the flame could not be formed at $\alpha_{NF} < 0.05$ at any decomposition reactions scheme.

Calculations of the temperature and concentration profiles in the flame of HNF have been performed at pressures 0.4, 0.1, and 5.0 atm. The results of calculations are presented below and compared with experimental data [1,4,15]. The coordinate x corresponds to the distance from the burning surface.

It has to be noted that available experimental data are very restricted in volume and have significant scatter. Correct comparison of theoretical and experimental results regarding temperature profile in burning HNF is hampered by the fact that the W/Re thermocouples used could not survive (burn out) at high temperatures in the flame of HNF. For this reason it is difficult to adequately treat the thermocouple readings at the temperatures higher than 1300-1500 K. In particular, observed bends in T(x) curve at pressures 0.4 – 1 atm may be attributed not only to the two-stage combustion of HNF but also to additional heating due to thermocouple material reaction with oxidizer containing species in the HNF flame.

The calculated T(x) data can be easily matched with experimental ones at relatively low temperatures, i.e. close to the burning surface. The noticeable difference between theoretical and experimental T(x) curves at pressures 0.4-1 atm and temperatures higher than 1300 K cannot be eliminated by reasonable variation of the kinetic constants in the chosen set of elementary reaction steps. Final validation of the chemical mechanism in the HNF flame takes special efforts directed to obtaining reliable independent data on the temperature and species concentrations.

It has to be noted that the bend in the T(x) curve disappears at a pressure of 5 atm, where the theoretical T(x) corresponds fairly well to the experimental one.

The calculated temperature and species concentration profiles in the HNF flame at atmospheric pressure are presented in Figs. 1-3. The multiple stages of the chemical reactions in the flame are the result of the complex structure of the HNF molecule and great variety of its decomposition products.

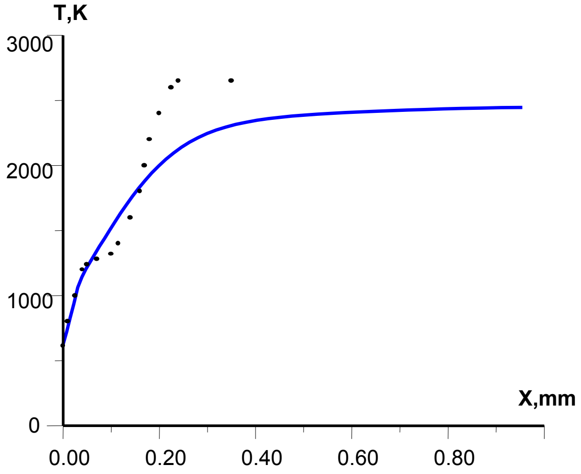

Fig. 1. Calculated temperature profile in the flame of HNF, P = 1 atm; T_s = 623 K; m = 1.232 kg/m^{2}s; Set # 1. Dots – experimental data [4].

The comparison of calculated and experimental [1] data on species profiles is presented in Figs. 2,3. In total, the agreement between the data is reasonable. However, there are some discrepancies, which have to be discussed. In particular, the calculated values for H_2O and N_2 concentrations agree within 30-50% error with the experimental values [1] but, in contrast to experiment, the calculated concentrations of H_2O exceed those of N_2.

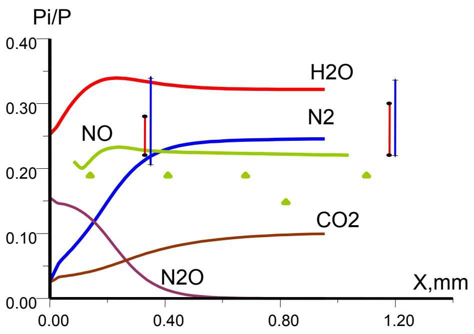

Fig.2. Species mole fraction distributions in the flame of HNF, P = 1 atm, Set # 1, T_s = 623K, m = 1.232 kg/m^{2}s; • → H_2O; + → N_2; Δ → NO. Dots – experimental data [1], vertical lines for H_2O and N_2 correspond to the experimental error estimations by [15].

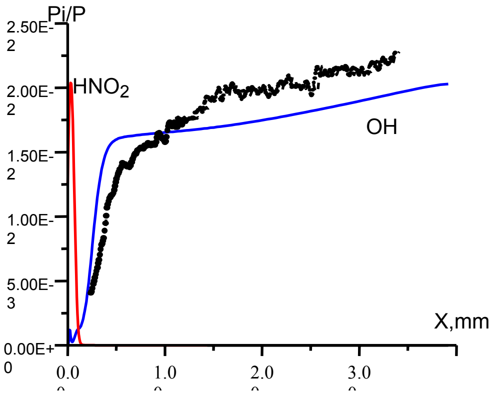

Fig. 3. HNO_2 and OH mole fraction distributions in the flame of HNF, P = 1 atm, Set # 1. T_s = 623K, m = 1.232 kg/m^{2}s. Dots – experimental data [1].

Figure 4 represents the results of calculations at a pressure of 5 atm performed with the set ≠1 at T_s = 680 K and m = 5.28 kg/m^{2}s [4]. It is seen that the calculated temperature profile reproduces the experimental one fairly well [4]. The variation of the reaction kinetics constant describes the elementary step

$$(15) NH_3 + OH = NH_2 + H_2O.$$

Analysis of the calculation results shows that the reactions of nitroform with hydrazine and partially with ammonia close to the burning surface provide heat generation sufficient for rising the temperature in the gas from T_s (~615 K) to about 1300 K. The further rise of temperature is owed to the reactions in the gas mixture consisted of NH_3, NO, NO_2, HNO_2, HCNO, N_2O, and CO.

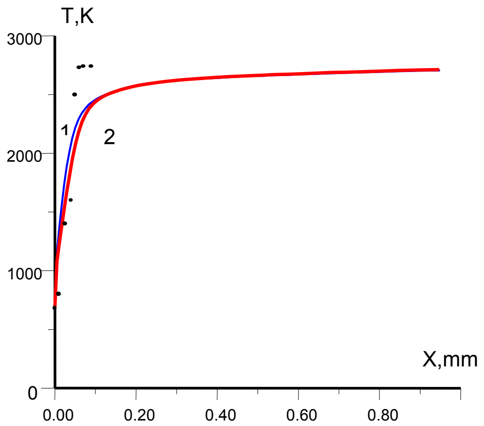

Fig. 4. Temperature distribution in the flame of HNF, P = 5 atm, Set # 1; T_s=680K, m=5.28 kg/m^{2}s. Dots – experimental data [4]. Curve 1 stands for $K_{15} = 2 \cdot 10^3 T^{2.04} \exp(-566/RT)$ and curve 2 for $K_{15} = 8 \cdot 10^5 T^{1.05} \exp(-700/RT)$.

Conclusions

1. The known HNF combustion mechanism [3] is based on assumption of evaporation and following decomposition of the HNF molecule in the gas phase. However, there are not unambiguous evidences of this assumption ($HNF_{liq} \rightarrow HNF_{gas}$) but some estimations point out on dissociative evaporation step in the form: $HNF_{liq} \rightarrow [(N_2H_4 + HC(NO_2)_3]_{liq} \rightarrow [N_2H_4 + HC(NO_2)_3]_{gas}$.
2. In the present work, the detailed kinetic mechanism is formulated for the reactions in the flame of HNF, which reasonably well describes experimentally recorded temperature and species profiles. This mechanism is based on the assumption that the reactions in the the condensed phase are well developed and, in addition, the HNF partially evaporates by the

way of dissociation into N_2H_4 and $HC(NO_2)_3$ in the liquid state.

3. The different channels for monomolecular decomposition of $HC(NO_2)_3$ are examined. The kinetic schemes are developed under assumption of the limiting stage described by the reaction $HC(NO_2)_3 \rightarrow NO_2 + HC(NO_2)_2$.

4. The calculations performed clearly show that the driving force for initial temperature rise in the gas phase just near the burning surface is the decomposition of nitroform followed by exothermic reactions between the nitroform and hydrazine and, partially, ammonia. These last reactions provide a temperature rise up to about 1300-1500K. The succeeding increase in the temperature is the result of exothermic reactions, which proceed in the gas mixture $H_2O/N_2/N_2O/NH_3/NO/NO_2/HNO_2/CO/CO_2/HCNO/HCN$.

5. Substantiation of the kinetic mechanism developed for the reactions in the HNF flame has to be continued. It takes special efforts on investigating the kinetic parameters of the elementary reactions with participation of $HC(NO_2)_3$ and N_2H_4 and their fragments and calculating the thermodynamic parameters of numerous species – intermediates.

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