This article was downloaded by: [Institute of Chemical Kinetics & Combustion - Siberian Branch] On: 14 October 2012, At: 21:38 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Combustion Theory and Modelling Publication details, including instructions for authors and subscription information:

http://www.tandfonline.com/loi/tctm20

A numerical study of the superadiabatic flame temperature phenomenon in HN₃ flames

Oleg P. Korobeinichev $^{\rm a}$, Alexander A. Paletsky $^{\rm a}$, Tatyana A. Bolshova $^{\rm a}$ & Vadim D. Knyazev $^{\rm b}$

^a Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia

^b Department of Chemistry, The Catholic University of America, Washington, DC, 20064, USA

Version of record first published: 02 Aug 2012.

To cite this article: Oleg P. Korobeinichev, Alexander A. Paletsky, Tatyana A. Bolshova & Vadim D. Knyazev (2012): A numerical study of the superadiabatic flame temperature phenomenon in HN_3 flames, Combustion Theory and Modelling, 16:5, 927-939

To link to this article: <u>http://dx.doi.org/10.1080/13647830.2012.687458</u>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <u>http://www.tandfonline.com/page/terms-and-conditions</u>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.



A numerical study of the superadiabatic flame temperature phenomenon in HN₃ flames

Oleg P. Korobeinichev^{a*}, Alexander A. Paletsky^a, Tatyana A. Bolshova^a and Vadim D. Knyazev^b

^aInstitute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia; ^bDepartment of Chemistry, The Catholic University of America, Washington, DC 20064, USA

(Received 1 April 2011; final version received 2 April 2012)

The phenomenon of superadiabatic flame temperature (SAFT) was discovered and investigated in a low-pressure HN_3/N_2 flame using numerical modelling. A previously developed mechanism of chemical reactions in the HN_3/N_2 flame at the pressure 50 Torr and the initial temperature $T_0 = 296$ K was revised. Rate constants of several important reactions involving HN_3 (HN_3 ($+N_2$) = N_2 + NH ($+N_2$), R1; HN_3 ($+HN_3$) = N_2 + NH $(+HN_3)$, R2; HN₃ + H = N₂ + NH₂, R4; HN₃ + N = N₂ + NNH, R5; and HN₃ + NH₂ = $NH_3 + N_3$, R7) were calculated using quantum chemistry and reaction rate theories. Modified Arrhenius expressions for these reactions are provided for the 300–3500 K temperature range. Modelling of the flame structure and flame propagation velocity of the HN₃/N₂ flame at p = 50 Torr and $T_0 = 296$ K was performed using the revised mechanism. The results demonstrate the presence of the SAFT phenomenon in the HN_3/N_2 flame. Analysis of the flame structure and the kinetic mechanism indicates that the cause of SAFT is in the kinetic mechanism: exothermic reactions of radicals with hydrogen atoms occur in the post flame zone, which results in the formation of super equilibrium H₂ concentrations. The flame propagation velocity is largely determined by the second-order HN_3 decomposition reaction and not by the reaction of HN_3 with H. as was previously assumed. Calculation of the flame propagation velocity according to the Zeldovich-Frank-Kamenetsky theory with the decomposition reaction as a limiting stage yielded a value that agrees with that obtained in numerical modelling using the complete reaction mechanism.

Keywords: hydrogen azide; superadiabatic flame temperature; flame speed; flame structure; reaction mechanism

1. Introduction

The phenomenon of superadiabatic flame temperature (SAFT) occurs when the maximum temperature in the front of the flame exceeds the adiabatic equilibrium temperature value. This phenomenon is of great interest, both from the fundamental and the practical standpoints. The fundamental interest is related to the physical and chemical causes of the occurrence of SAFT, and the practical interest is due to the fire and explosion safety concerns in design and operation of industrial devices using combustible gases.

The phenomenon of superadiabatic flame temperature has been observed in rich hydrocarbon flames (the C-H-O system) [1] and described in number of articles [1–6]. In reference

^{*}Corresponding author. Email: korobein@kinetics.nsc.ru

[1], where modelling of flame structure was used, this phenomenon was shown to be related to formation of super equilibrium concentrations of certain hydrocarbon species and water in the chemical reaction zone in the flame, and to be accompanied by heat consumption in endothermic reactions in the post-flame zone as the system approaches thermodynamic equilibrium. In rich methane-oxygen flames [4], apart from the reaction mechanism and chemical kinetics, an essential role in causing the superadiabatic phenomenon is played by the diffusion of hydrogen atoms into the fresh mixture zone and by the formation of super equilibrium concentrations of water in the chemical reaction zone.

The practical importance of the information on SAFT occurrence in flames is discussed in the book by Razlovsky [7]. Appearance of a maximum temperature in the flame front stabilises the flames of rich mixtures of critical composition, which leads to the expansion of the upper concentration limit in the propagation of flames in C-H-O compound mixtures. The upper concentration limit appearing in the studies of flame propagation of fuel-rich mixtures is a very important property directly related to the safety of handling of combustible gases. Therefore, studies of the SAFT phenomenon are directly linked to practical applications in the field of prevention of industrial accidents.

Unlike the flames in which flame propagation is determined by chemical reactions between the oxidiser and the fuel, there is a class of self-sustained decomposition flames, such as, for example, decomposition flames of acetylene (C_2H_4) [8], hydrazine (N_2H_4) [9], and hydrogen azide (HN₃) [10]. The latter two of these compounds are well known representatives of high energy N/H based substances.

The study of reference [9] reported experimental data on the flame structure of hydrazine vapour decomposition at the pressure of 14 Torr and the initial temperature of 80°C. The N₂H₄ decomposition flame at the distance of 20 mm from the burner surface exhibited thermodynamically non-equilibrium composition of products: in addition to hydrogen and nitrogen, which are the main equilibrium combustion products, the flame contained large amount of ammonia (~0.45 mole fraction). The adiabatic flame temperature corresponding to this composition of products in front of the flame should be equal to 1700 K [9], which by far exceeds the equilibrium value of 1340 K. An attempt to measure the maximum flame temperature by a thermocouple shielded by a quartz capillary yielded the value of 1350 K; in the authors' opinion [9], the actual value is much higher, presumably due to the errors of thermocouple measurements. This higher value would serve as a manifestation of the superadiabatic effect in the hydrazine flame.

Until recently, no data on the presence of the superadiabatic phenomenon in the flame of hydrogen azide, another representative of the N-H system, was available in the literature. In 2009, we reported observation of superadiabatic flame temperature in our numerical study of the structure and the speed of the hydrogen azide decomposition flame [11].

The interest in the flame of hydrogen azide is also related to its being an important intermediate in the decomposition and combustion of a highly energetic condensed phase compound: 5-aminotetrazole [12]. No mechanism of combustion of 5-aminotetrazole is available in the literature. The kinetic mechanism of HN₃ decomposition developed in the current study can be used as a subset within a more complex detailed mechanism of a C-H-N system. As an example, one can offer reference [13], in which a model of combustion of nitrocellulose doped with HN₃ was developed; in that model, HN₃ was considered as a product of pyrolysis of 5-aminotetrazole. The authors of [13], using the existing literature data on the kinetics of HN₃ decomposition, obtained a disagreement between numerical modelling and their experimental data on the flame structure of a model mixture: $H_2/O_2/Ar/HN_3$. The kinetic mechanism used in [13] was based on a literature review, and the observed disagreement is related to the profile of HN₃ consumption. The

mechanism of HN_3 decomposition developed in the current study is likely to help to clarify the chemical mechanisms of HN_3 and related intermediates behaviour in this and other similar chemical systems.

A detailed investigation of SAFT becomes possible only as a result of the development of modern computational technology and detailed kinetic mechanisms of the involved chemical systems. Prior to that, all attempts at explanations of the phenomenon were mere suggestions. It is impossible to predict SAFT without performing experiments or detailed modelling of the flame structure. Computer modelling is a powerful tool of research of the kinetic features of combustion systems, which enables prediction of their behaviour at varying initial conditions. It also enables prediction of new effects that often cannot be characterised experimentally.

The objective of the current work was to perform a numerical study of the phenomenon of the superadiabatic flame temperature in the hydrogen azide flame at low pressure, and to analyse its causes by modelling the flame structure using a detailed kinetic mechanism of the combustion process. As the superadiabatic effect depends on the kinetic mechanism adopted, which so far has been insufficiently studied, the first step was to analyse the reaction mechanism and to evaluate the rate constants of the most important constituent reactions including advanced quantum chemistry and reaction rate theory methods. Satisfactory agreement between the available experimental data on the flame speeds in the mixtures of hydrogen azide and nitrogen of varying concentrations and the results of modelling based on this mechanism testify to the reliability of the developed mechanism and the associated rate constant values.

2. Results and discussion

2.1 Description of the mechanism and calculations of the rate constants of the reactions involving hydrogen azide

Reference [11] presented a mechanism that provided a satisfactory description of the existing experimental data on self-ignition limits and flame speeds in the mixtures of HN₃ with N₂. The mechanism included reactions with participation of HN₃, for which rate constant values were obtained either via extrapolation of the low-temperature experimental data to a higher temperature range (\sim 1500–3500 K), or from earlier BEBO (Bond Energy Bond Order) estimates [14]. In the current work, rate constants of four key reactions (HN₃+M = NH+N₂+M (M = N₂, HN₃, Ar), HN₃+N = N₂+NNH, HN₃+H = N₂+NH₂, and HN₃+NH₂ = NH₃+N₃) over the 300–3500 K temperature range were obtained in a computational study. The results of this computational study are presented in Table 1 and are discussed below. The rate constant of reaction R6, HN₃+NH = NH₂+N₃, was taken from an earlier computational work [15].

2.2 The computational study of the reactions involving HN_3

The rate constants of reactions R1–R3 (see Table 1 for reaction numbering) were obtained by using the Master Equation model of reference [16], which was developed on the basis of earlier experimental and theoretical studies of this reaction. Decomposition of hydrogen azide proceeds via formation of the NH biradical in a triplet or a singlet state and N₂. The triplet channel is predominant and the contribution of the singlet channel is minor under most conditions. In the current work, the singlet channel is thus neglected; the rate constants given for reactions R1–R3 are those of the overall reaction. In reference [16], two versions of the temperature dependence of the critical energy transfer parameter, $\langle \Delta E \rangle_{down}$,

№	Reaction	А	n	Ea	
R1	$HN_3 + N_2 = N_2 + NH + N_2$	2.14×10^{26}	-2.970	195151	
R2	$HN_3 + HN_3 = N_2 + NH + HN_3$	6.67×10^{26}	-2.863	201280	
R3	$HN_3 + Ar = N_2 + NH + Ar$	7.55×10^{25}	-3.001	191551	
R4	$HN_3+H = N_2+NH_2$	3.71×10^{7}	1.878	13754	
R5	$HN_3 + N = N_2 + NNH$	1.87×10^{8}	1.512	14500	
R6 ^a	$HN_3 + NH = NH_2 + N_3$	7.83×10^{2}	3.19	41700	
R7	$HN_3 + NH_2 = NH_3 + N_3$	5.88	3.483	-2900	

Table 1. Kinetic mechanism of HN₃ decomposition.

Note: Units are cm³, mole, s, J, and K.

 $k = AT^{n}exp(-E_{a}/RT), T = 300-3500 K.$

 $^{a}T = 300-2000 \text{ K}.$

for collisions between HN₃ and argon bath gas were used in fitting of the experimental data: the temperature independent version (resulting in $\langle \Delta E \rangle_{down}(Ar) = 349 \text{ cm}^{-1}$), and the proportional version (resulting in $\langle \Delta E \rangle_{down}(Ar) = 0.217 \times T \text{ cm}^{-1} \text{ K}^{-1}$). In the current work, we use the model of reference [16] with the proportional temperature dependence of $\langle \Delta E \rangle_{down}$, which, at the pressure of 50 Torr, results in the modified Arrhenius parameters given in Table 1 for Ar bath gas. The values of $\langle \Delta E \rangle_{down}$ for N₂ and HN₃ bath gases are, however, unknown. Experimental and modelling data on unimolecular reactions of small hydrocarbons indicate that it is reasonable to expect $\langle \Delta E \rangle_{down}(N_2)$ to be similar to or somewhat larger than $\langle \Delta E \rangle_{down}(Ar)$ (e.g., [17–20]), and $\langle \Delta E \rangle_{down}$ of a polyatomic collider larger by a factor of, perhaps, 2–4. However, in the case of a polar molecule such as HN₃, one can reasonably expect an enhancement of the HN₃ – N₂ interaction. Similarly, interactions between two HN₃ molecules are expected to be more attractive compared to interactions between hydrocarbon molecules because of a possibility of hydrogen bond formation. Stronger intermolecular interactions are likely to result in more efficient collisional energy transfer.

To investigate the possibility of a more effective collisional energy transfer in the cases of N₂ and HN₃ bath gases, quantum chemical calculations of intermolecular interactions in the HN₃…N₂ and HN₃…HN₃ complexes were performed. The CCSD(T)//BH&HLYP and CCSD(T)//CCSD methods (all with the aug-cc-pvdz basis set) were used; the energy values quoted below are those obtained with the latter method; the differences between the two methods are less than $0.7 \text{ kJ} \text{ mol}^{-1}$. Here, CCSD denotes coupled-clusters theory with singles and doubles; additional (T) in the notation stands for non-iterative inclusion of triples. BH&HLYP stands for density functional method using Becke's half-and-half nonlocal exchange with the Lee, Yang, and Parr correlation functional. The results indicate that N_2 and HN_3 can form a weakly bound complex with 4.6 kJ mol⁻¹ binding energy, in which the lone pair of N_2 interacts with the H atom of the HN₃ molecule. In the case of $HN_3 - HN_3$ interaction, the binding energy is significantly larger (12.9 kJ mol⁻¹), which is caused by a hydrogen bond formation. In comparison, the binding energy of the $Ar - HN_3$ complex is only 2.8 kJ mol⁻¹. Formation of molecule—bath gas complexes upon collision that can survive for one or several vibrational periods is likely to result in more effective transfer of vibrational energy than in the case of purely impulsive collisions. An example of more effective collisional energy transfer in the case of hydrogen bond interaction within the collisional complex is given by the $H + O_2 \rightarrow HO_2$ reaction, where H_2O bath gas results in recombination reaction rates that are larger than those observed in inert gases by an order of magnitude [21]. The same reaction has rate constants in N2 bath gas that are larger than those in Ar bath gas by a factor of 2–3, with significantly larger values of $-\langle \Delta E \rangle_{all}$ and collision efficiency required to explain the differences using theoretical modelling [21,22]. In a different example, the rate constants of recombination of NH₂ in N₂ bath gas are 2–3 times larger than in Ar bath gas [23,24] and the rate constants in NH₃ bath gas are 10 times larger than in Ar [23].

Based on the study of the collision complexes and analogy with other reactions involving polar species, the following temperature dependent models of the collisional energy transfer for N₂ and HN₃ bath gases were used: $\langle \Delta E \rangle_{down}(N_2) = 0.40 \times T \text{ cm}^{-1} \text{ K}^{-1}$, and $\langle \Delta E \rangle_{down}(HN_3) = 1.60 \times T \text{ cm}^{-1} \text{ K}^{-1}$. The rate constants obtained using these models are larger than those for Ar bath gas. For N₂ bath gas, the difference is, on average, a factor of 2.6 in the 800–3500 K temperature range; for HN₃ bath gas, a factor of 13. These factors are in general agreement with the experimental effects of nitrogen and polar polyatomic colliders observed for the reactions of H addition to O₂ and NH₂ recombination, as discussed above. The resultant temperature dependences of the rate constants of reactions R1–R3 at 50 Torr are given in Table 1.

Reactions R4 and R5 were studied computationally using quantum chemistry and transition state theory. The molecular structures and vibrational frequencies of all species involved were calculated using the BH&HLYP/aug-cc-pvdz hybrid density functional method. Rate constants were calculated using transition state theory (with the barrier width-based Eckart tunnelling correction [25,26] in the case of reaction R4. The reaction energy barriers were adjusted to reproduce the experimental low-temperature rate constant values of reference [27]. The resultant temperature dependences (Table 1), thus, represent extrapolations of the experimental data to higher temperatures via transition state theory modelling.

No experimental data are available for reactions R6 and R7. Reaction R6 was studied theoretically by Henon and Bohr [15], who performed high-level electronic structure calculations and obtained rate constant values by applying transition state theory with tunnelling correction. The authors of reference [15] did not provide an analytical expression for the rate constant; the rate parameters given in Table 1 were obtained from reference [16], where the data of Henon and Bohr were fitted in the 800–2000 K temperature range. Reaction R7 was studied in the current work. The reaction potential energy surface was studied using the BH&HLYP/aug-cc-pvdz method for geometry optimisation and vibrational frequencies and the CCSD(T)/aug-cc-pvtz method for single-point energy calculations. Rate constants (Table 1) were calculated using transition state theory with the barrier width-based Eckart tunnelling correction [25,26]. Details of all quantum chemical and rate constant calculations, including short discussions of individual addition-decomposition pathways of reactions R4 and R5, are presented in the online Supplementary Material (Tables 1S and 2S).

2.3 Modelling

Modelling of the flame structure of 85% of HN₃ in nitrogen was performed using the revised mechanism ([28] and Table 3S in the online Supplementary Material), which is based on the mechanism of reference [11] but includes rate constants of reactions involving HN₃ (R1–R7) re-evaluated in the current study. The mechanism consists of 61 reactions with the participation of 14 species: H₂, H, N, NH, NH₂, NNH, NH₃, HN₃, N₃, N₂, Ar, N₂H₂, N₂H₃, and N₂H₄. The thermodynamic parameters and the transport properties for most species were taken from reference [29]. The transport properties of N₃ and HN₃ were evaluated by using Lennard – Jones coefficients of structurally similar C-N compounds and the thermodynamic parameters were taken from reference [30]. Calculations were



Figure 1. Flame speed in HN_3/N_2 mixtures at p = 50 Torr and $T_0 = 296$ K as a function of HN_3 mole fraction. Symbols: data of reference [10]; line: modelling results.

performed using PREMIX and EQUIL codes from the package CHEMKIN-II [31]. The size of the calculated area in PREMIX code was from -5 to 15 cm or from -5 to 100 cm.

2.4 The velocity of HN₃ flame propagation

The experimental data [10] and the results of calculating the dependence of the velocity of HN₃ flame propagation (U) on HN₃ concentration at the pressure of 50 Torr and the initial temperature of 296 K obtained with the revised mechanism presented in this study are shown in Figure 1. The flame propagation velocity increases from ~ 2 m/s to ~ 10 m/s with the increasing concentrations of HN₃ in nitrogen (from 30 to 100%). The results of the calculations are in satisfactory agreement with the experimental data.

The sensitivity analysis of the flame speed performed using the current mechanism (Figure 2) reveals a dependence of the flame speed on the rate constants of reactions with the participation of HN₃ (R1, R2, R6) and the NH and the NH₂ radicals (R20, R16). As can be seen from the lower plot in Figure 3, NH and NH₂ have the highest concentrations in flame among radicals. The maximum relative change of the flame speed reaches $\sim 12\%$ with the variation of the rate constant of reaction R2 by a factor of 5. Rate constants of other reactions exert 2–4 times less influence.



Figure 2. Sensitivity analysis of flame speed.



Figure 3. Structure of the HN₃/N₂ (85/15 vol%) flame at p = 50 Torr and $T_0 = 296$ K.

2.5 HN_3/N_2 flame structure

Modelling the structure of the HN_3/N_2 flame at the pressure of 50 Torr indicated that for all initial HN_3 concentrations, the highest temperature in the flame front exceeds the adiabatic equilibrium value. It should be noted that there are no data in literature that would testify to experimental observations of this phenomenon for HN_3 flames. A description of the flame structure and explanation of the causes of the phenomenon of superadiabatics is given below for the mixture of 85% HN_3 with 15% N_2 .

The modelling results showing temperature profiles and concentration profiles of the main stable species and radicals are given in Figure 3. The width of the flame zone in which consumption of HN₃ is completed is about 0.1 cm. The flame temperature reaches the adiabatic value ($T_{ad} = 2939$ K) and begins to exceed it, starting with the distance ~0.1 cm from the origin of coordinates. The maximum elevation of the temperature above the adiabatic value amounts to 795 K and is reached in the flame at the distance ~0.8 cm (Figure 3) from the origin of coordinates. The profiles of all radical and atom concentrations, except for that of the H atoms, reach their maxima in the zone of chemical reactions. Concentration of the H atoms increases across the entire zone. Ammonia is the first intermediate product to emerge. Among polyatomic radicals, NH and NH₂ have the highest concentrations in the flame, with values reaching maxima (~0.04 mole fraction) at the distance of ~0.095 cm. It can be seen from the plots that when the concentrations of NH and NH₂ in the flame reach their maxima, the temperature approaches the equilibrium value. Further growth of the flame temperature is accompanied by the reduction in NH₃, NH₂, and NH concentrations.

It can be seen from Figure 3 and Table 2 that, already at the distance of 2 cm, practically all the nitrogen-containing species and radicals are consumed and their concentrations approach equilibrium values. The mass fraction of N_2 in 1 mole of the gas mixture,

Table 2. The species composition (in mole fraction - α_i) and temperature at the distance of 2 cm from the origin of coordinates in the 0.85HN₃/0.15N₂ flame and in equilibrium.

	N_2	H_{2}	Н	NH	NH ₃	NH ₂	$MW_{mix} \\$	T, K
Modeling (2 cm) Equilibrium	0.741 0.7	0.196 0.121	0.06 0.176	$ \begin{array}{c} 6.9\!\times\!10^{-4} \\ 1.5\!\times\!10^{-6} \end{array} $	$2.8 \times 10^{-4} \\ 1.7 \times 10^{-8}$	$ \begin{array}{c} 3.8\!\times\!10^{-4} \\ 8.8\!\times\!10^{-8} \end{array} $	21.2 20.03	3710 2939

calculated as $\alpha_{N2} \times MW_{N2}/MW_{mix}$ (here, α_{N2} is the mole fraction of N₂ in the mixture, MW_{N2} is the molecular weight of N₂, and MW_{mix} is the molecular weight of the mixture) equals 0.979, which coincides with its value at T_{ad}.

It can also be seen that the H_2 and H concentrations at the distance of 2 cm (Table 2, Figure 3) significantly differ from their corresponding equilibrium values. The calculated concentration of H_2 exceeds its equilibrium value. At the distance of ~100 cm from the flame front, the temperature decreases by ~500 K and H_2 concentration decreases to 0.15 mole fraction, whereas H concentration increases to 0.14 mole fraction.

2.6 Superadiabatics in HN₃ flame

Analysis of the flame structure indicates that superadiabatics in the HN₃ flame is accompanied by the presence of super equilibrium concentrations of molecular hydrogen in the post-flame zone at the distance of ~ 0.8 cm from the origin of coordinates. As can be seen from Figure 4, in the zone located between 0.8 and 100 cm, endothermic reactions take place, which results in the decrease of flame temperature, also a characteristic feature of the SAFT phenomenon in flames. Dissociation of molecular hydrogen is one of these endothermic reactions. Analysis of the dependence of the heat release rate on the flame temperature and the distance from the origin of coordinates demonstrates the presence of several heat release stages across the flame (Figure 5). In the low-temperature flame zone (T \sim 400–1200 K), minor heat release is caused by the radicals recombination reactions (-R24) $NH_2+H+M \Rightarrow NH_3+M$, (-R36) $NH+NH+M \Rightarrow N_2H_2+M$, (-R42) $N_2H_2+H+M \Rightarrow N_2H_3+M$, and (-R52) $NH_2+NH_2+M = N_2H_4+M$. The maximum heat release rate is observed at T = 600-700 K. Further on, these reactions do not exert any significant influence. Most of the heat release occurs in the subsequent second and third stages, in reactions of hydrogen atoms with other species. About half of the total heat is released in the second stage in the reaction R4 (H + HN₃); the other half is released in the third stage, primarily in the reactions of radical recombination with the H atoms (R12, R13, R16, R18, R19, R20, R24, R28, R37, R42, R60) (see Table 3S in the online Supplementary Material). The maximum values of the heat release rates in the second and the third stages, occurring at the temperatures of \sim 2200 K and \sim 2500 K, are similar in values: \sim 6 kJ cm⁻³ s⁻¹ and \sim 5.2 kJ cm⁻³ s⁻¹, respectively. Therefore, to analyse the reaction mechanism and to develop a scheme of H₂ formation, the temperature range of 2200-2500 K was chosen.

To reveal specific features of the developed kinetic mechanism, an analysis of reactions with the participation of HN_3 was performed. Analysis of the HN_3 consumption rates in reactions (R1–R7) during flame propagation shows that hydrogen azide is consumed in the low-temperature flame zone (from 300 to 1000–1200 K) via reactions R4 ($HN_3+H = NH_2+N_2$) and R7 ($HN_3+NH_2 = NH_3+N_3$). Reaction R4 provides the major contribution: the maximum HN_3 consumption rate in R7 is 5 times lower than that in reaction R4. The HN_3 decomposition rate in reactions R1 and R2 becomes noticeable only at the temperature



Figure 4. Temperature and heat release profiles in the HN_3/N_2 (85/15 vol%) flame at 50 Torr.

of \sim 1200 K. The HN₃ consumption rates in reactions R1, R2, and R4 have their maxima within the temperature range of \sim 2100–2500 K.

Thus, this kinetic scheme indicates that the temperature range of the maximum HN_3 consumption rate coincides with the temperature range of the maximum heat release rate in the flame in all the reactions. The subset of reactions responsible for the formation of H_2 in the flame does not change over the 2000–3000 K temperature range, although relative contributions of individual pathways vary with temperature. The scheme of hydrogen molecules formation at the temperature of 2200 K is given in Figure 6. Reactions presented in the scheme are responsible for formation of the major part (96%) of the total concentration of H_2 . Hence, this scheme almost fully describes the process of formation of the super equilibrium H_2 concentrations in the flame. Reactions R12, R37, and R18 occur with consumption of the H atoms. The total heat release in these reactions except R4. Thus, the main cause for the occurrence of the superadiabatics phenomenon in the flame is the heat release in exothermic reactions, mainly those with the participation of H atoms; these reactions form super equilibrium concentrations of H_2 molecules.



Figure 5. Heat release profiles across the HN₃/N₂ (85/15 vol%) flame at 50 Torr.



Figure 6. The scheme of H_2 formation in the HN₃ flame at T = 2200 K.

2.7 The influence of the H_2 and H diffusion coefficients on the SAFT

Changing the collision parameters (input data for the TRAN code [31]) allows the values of D(H) diffusion coefficient of H atoms in the fuel mixture to be changed and its influence on the SAFT to be determined. Calculations of D(T₀,H), using package CHEMKIN-II [31] for the binary H-N₂ diffusion coefficient at p = 50 Torr and $T_0 = 296$ K provided the diffusion coefficient value for the mixture 85%HN₃ + 15%N₂ equal to D(T₀,H) = 15.0 cm² s⁻¹. To study the effect of H atom diffusion on the maximum flame temperature, computations were performed for the case of a fuel-rich mixture with the values of the diffusion coefficients of H atoms and H₂ molecules artificially lowered to that of N₂ (D(T₀,N₂) = 2.45 cm² s⁻¹ at 50 Torr and 296 K). Thus, D(T,H) was decreased by a factor of six. This computational exercise resulted in the reduction of the maximum flame temperature by only ~10 K, or 1.5% of the total temperature elevation above the adiabatic equilibrium value (Figure 7). Decreasing the diffusion coefficient of the hydrogen atom also leads to a reduction of the flame propagation velocity by ~9%. These results lead to the conclusion that the diffusion of H or H₂ does not cause the effect of SAFT in HN₃ flames.



Figure 7. The HN_3/N_2 (85/15 vol%) flame temperature profile at 50 Torr obtained in calculations with different values of diffusion coefficients.

2.8 The flame reaction mechanism and the flame propagation velocity

The authors of reference [27] advanced a hypothesis that reaction R4 (HN₃+H = N₂+NH₂) plays an important role in flame propagation. However, the sensitivity analysis of the flame propagation velocity performed in the current work shows that it is not R4 but rather the reactions of HN₃ decomposition (R1–R2) that determine the flame propagation velocity, despite being endothermic. Between R1 and R2, given the high HN₃ concentrations in the HN₃/N₂ mixtures, it is the faster reaction HN₃ (+HN₃) = N₂ + NH (+HN₃) (R2) that plays the major role in the consumption of HN₃. The effect of reactions R2 and R4 on the flame velocity can be understood by considering a simplified reaction scheme, consisting of the following two stages.

$$A + M \xrightarrow{\kappa_2} \cdots \rightarrow C + Products$$
 (-Q₁)

(Stage 1)

 $A + \overset{k_4}{C} \rightarrow B + Products \qquad (+Q_2)$

(Stage 2)

Here, A is HN₃, C is H, M – a third body, B – reaction products, Q₁ and Q₂ are the reaction heat values, and k_2 and k_4 are the rate constants of reactions R2 and R4 in Table 1. Stages (1) and (2) are endothermic and exothermic, respectively. This scheme implies that, at the endothermic stage 1, production of NH in reaction 2 is followed by subsequent fast reactions resulting in the formation of H, which further react equally fast with the original reactant HN₃ at the exothermic stage 2. This sequence is followed by subsequent fast reactions, resulting in the formation of the final reaction products and in heat release. Such a multi-step reaction regime has been described by Zeldovich et al. as a "merging" regime type [32].

We calculated the flame propagation velocity in the 85/15 vol% HN_3/N_2 mixture at 50 Torr and $T_0 = 296$ K within the framework of the "merging" regime of reference [32] using the bimolecular reaction R2 with $M = HN_3$ as the limiting stage. The second-order of the reaction for the HN_3/N_2 flame has been confirmed by the experimental dependence of the flame propagation velocity on pressure [10]. Calculations were performed using the expression from reference [32]:

$$S_{u}^{2} = \frac{4\lambda_{b}ka_{0}}{\rho_{0}c\left(T_{b} - T_{0}\right)^{3}} \left(\frac{T_{0}}{T_{b}}\right)^{2} \left(\frac{RT_{b}^{2}}{E}\right)^{3}$$
(1)

where S_u is the linear burning velocity (cm s⁻¹) with respect to the unburnt gas; λ_b is the thermal conductivity $\lambda_b = \lambda(T_b)$; a_0 is the initial concentration of reactant (HN₃); ρ_0 and c are the density and the constant pressure heat capacity of the mixture; and $k = k_0 e^{-E/RT_b}$ is the rate constant of the limiting stage with $T = T_b$. According to the Zeldovich and Frank-Kamenetsky theory [32], the value of T_b ("combustion" temperature) used in Equation (1) is very close to the adiabatic flame temperature (T_{ad} \approx 2940 K for the 0.85/0.15 HN₃/N₂ mixture in our work). In the calculations, the following numerical values were used: $\lambda_b = 2.8 \times 10^{-3}$ J cm⁻¹ K⁻¹ s⁻¹ [31], $k = 2.03 \times 10^{13}$ cm³ mol⁻¹ s⁻¹; c = 44.4 J mol⁻¹ K⁻¹ [31], E = 160.57 kJ mol⁻¹, $a_0 = 0.85\rho_0$. The resultant value of the flame propagation velocity, $S_u = 470$ cm s⁻¹ at $T = T_{ad}$ is lower than both the experimental value (~850 cm s⁻¹ [10])

and the result of the full mechanism simulation. However, using the superadiabatic flame temperature value (3700 K) obtained in kinetic simulations for T_b resulted in Equation (1) yielding the flame speed $S_u = 850$ cm s⁻¹. The latter value is in good agreement with the calculations of the flame propagation velocity made using the PREMIX code with the complete reaction mechanism. These results support a suggestion that the appropriate value for temperature T_b in Equation (1) for the flame propagation velocity is that of the maximum temperature in the flame front, which may exceed the adiabatic temperature value.

3. Conclusions

A mechanism of chemical reactions in the HN_3/N_2 flame at the pressure of 50 Torr is presented. Rate constants of important reactions involving HN_3 were calculated using quantum chemistry and reaction rate theories. Modelling of the flame structure and flame propagation velocity of the HN_3/N_2 flame was performed.

Based on the analysis of the flame structure, the phenomenon of superadiabatic flame temperature (SAFT) in HN_3/N_2 flames was discovered and investigated. Analysis of the data obtained indicates that the cause of SAFT is in the kinetic mechanism of the overall reaction; formation of super equilibrium H_2 concentrations occurs in the post flame zone as a result of exothermic reactions of radicals with hydrogen atoms.

Analysis of the data obtained in modelling indicated that the flame propagation velocity is largely determined by the second-order HN_3 decomposition reaction and not by the reaction of HN_3 with H, as was previously assumed. A calculation performed using the Zeldovich-Frank-Kamenetsky theory with the decomposition reaction as the limiting stage yielded a value of the flame propagation velocity that agrees with that obtained in numerical modelling using the complete reaction mechanism.

Acknowledgments

V. D. Knyazev acknowledges partial support of his contribution by the Ministry of Science and Education of the Russian Federation under Contract 02.740.11.5176.

References

- F. Liu, H. Guo, G.J. Smallwood, and Ö.L. Gülder, Numerical study of the superadiabatic flame temperature phenomenon in hydrocarbon premixed flames, Proc. Combust. Inst. 29 (2002), pp. 1543–1550.
- [2] K.E. Bertagnolli and R.P. Lucht, Temperature profile measurements in stagnation-flow, diamond-forming flames using hydrogen CARS spectroscopy, Proc. Combust. Inst. 26 (1996), pp. 1825–1833.
- [3] F. Liu and Ö.L. Gülder, Effect of pressure and preheat on super-adiabatic flame temperatures in rich premixed methane/air flames, Combust. Sci. Technol. 180 (3) (2008), pp. 437–452.
- [4] F. Liu and Ö.L. Gülder, Effects of H₂ and H preferential diffusion and unity lewis number on superadiabatic flame temperatures in rich premixed methane flames, Combust. Flame 143 (2005), pp. 264–281.
- [5] E. Meeks, R.J. Kee, D.S. Dendy, and M.E. Coltrin, Computational simulation of diamond chemical vapor decomposition in premixed C₂H₂/O₂/H₂ and CH₄/O₂—strained flames, Combust. Flame 92 (1993), pp. 144–160.
- [6] V.V. Zamashchikov, I.G. Namyatov, V.A. Bunev, and V.S. Babkin, On the nature of superadiabatic temperatures in premixed rich hydrocarbon flames, Combust. Explo. Shock 40 (2004), pp. 38–41.
- [7] A.I. Razlovsky, Fundamentals of Safety in Explosion Control in Handling Combustible Gases and Vapors, Khimiya, Moscow, 1980 (in Russian language).
- [8] G.A. Cummings, A.R. Hall, and R.A.M. Straker, Decomposition flames of acetylene and methyl acetylene, Proc. Combust. Inst. 8 (1962), pp. 503–510.

- [9] D.I. Maclean and H.G.G. Wagner, The structure of the reaction zones of ammonia-oxygen and hydrazine-decomposition flames, Proc. Combust. Inst. 11 (1967), pp. 871–878.
- [10] P. Laffitte, I. Hajal, and J. Combourieu, *The decomposition flame of hydrogen azide*, Proc. Combust. Inst. 10 (1965), pp. 79–85.
- [11] O.P. Korobeinichev, A.A. Paletsky, N.V. Budachov, T.A. Bolshova, and V.D. Knyazev. Book of Abstracts, Eighth International Symposium on Special Topics in Chemical Propulsion, Cape Town, South Africa, 2009.
- [12] A.A. Paletsky, N.V. Budachev, and O.P. Korobeinichev, *Mechanism and kinetics of the thermal decomposition of 5 aminotetrazole*, Kinet. Catal. 50 (2009) pp. 627–635. [Original Russian language publication: Kinetika i Kataliz 50 (2009), pp. 653–662.]
- [13] M.P. Gramsa, W.R. Anderson, and R.C. Sausa, An experimental and modeling study of ingredients for propellant for burn-rate enhancement, Proceedings of the Army Science Conference (26th), Orlando, Florida, 2008.
- [14] O. Kajimoto, T. Yamamoto, and T. Fueno, *Kinetic studies of the thermal decomposition of hydrazoic acid in shock waves*, J. Phys. Chem. 83 (1979), pp. 429–435.
- [15] E. Henon and F. Bohr, Comparative ab initio MO investigation on the reactivity of the three $NH(a^{1}\Delta)$, $NH(X^{3}\Sigma)$ and $NH_{2}(X^{2}B_{1})$ radical species in their bimolecular abstraction gas-phase reaction with the HN3 molecule, J. Mol. Struct. THEOCHEM 531 (2000), pp. 283–299.
- [16] V.D. Knyazev and O.P. Korobeinichev, *Thermal decomposition of HN₃*, J. Phys. Chem. A 114 (2010), pp. 839–846.
- [17] A. Bencsura, V.D. Knyazev, S.-B. Xing, I.R. Slagle, and D. Gutman, Kinetics of the thermal decomposition of the n-propyl radical, Proc. Combust. Inst. 24 (1992), pp. 629–635.
- [18] P.W. Seakins, S.H. Robertson, M.J. Pilling, I.R. Slagle, G.W. Gmurczyk, A. Bencsura, D. Gutman, and W. Tsang, *Kinetics of the unimolecular decomposition of isopropyl: Weak collision effects in helium, argon, and nitrogen*, J. Phys. Chem. 97 (1993), pp. 4450–4458.
- [19] V.D. Knyazev and W. Tsang, Chemically and thermally activated decomposition of secondary butyl radical, J. Phys. Chem. A 104 (2000), pp. 10747–10765.
- [20] A.A. Shestov, K.N. Popov, and V.D. Knyazev, Kinetics of the unimolecular decomposition of the 2-chloroallyl radical, J. Phys. Chem. 109 (2005), pp. 8149–8157.
- [21] J.V. Michael, M.-C. Su, J.W. Sutherland, J.J. Carroll, and A.F. Wagner, *Rate constants for H* + $O_2 + M \rightarrow HO_2 + M$ in seven bath gases, J. Phys. Chem. A 106 (2002), pp. 5297–5313.
- [22] R.X. Fernandes, K. Luther, J. Troe, and V.G. Ushakov, *Experimental and modelling study of the* recombination reaction $H + O_2$ (+M) \rightarrow HO₂ (+M) between 300 and 900 K, 1.5 and 950 bar, and in the bath gases M = He, Ar, and N₂, Phys. Chem. Chem. Phys. 10 (2008), pp. 4313–4321.
- [23] P.V. Khe, J.C. Soulignac, and R. Lesclaux, Pressure and temperature dependence of NH₂ recombination rate constant, J. Phys. Chem. 81 (1977), pp. 210–214.
- [24] V.A. Lozovskii, V.A. Nadtochenko, O.M. Sarkisov, and S.G. Cheskis, *Study of NH₂ radical recombination by intraresonator laser spectroscopy*, Kinet. Catal. 20 (1979), pp. 1118–1123.
- [25] V.D. Knyazev, A. Bencsura, S.I. Stoliarov, and I.R. Slagle, *Kinetics of the* $C_2H_3 + H_2 \rightarrow H + C_2H_4$ and $CH_3 + H_2 \rightarrow H + CH_4$ reactions, J. Phys. Chem. 100 (1996), pp. 11346–11354.
- [26] V.D. Knyazev and I.R. Slagle, *Experimental and theoretical study of the* $C_2H_3 \rightarrow H + C_2H_2$ *reaction. Tunneling and the shape of falloff curves*, J. Phys. Chem. 100 (1996), pp. 16899–16910.
- [27] G. Le Bras and J. Combourieu, *The reactions of atomic hydrogen and active nitrogen with hydrogen azide*, Int. J. Chem. Kinet. 5 (1973), pp. 559–576.
- [28] Kinetics mechanism of HN₃ decomposition (2010), Web site of Laboratory of Kinetics of Combustion Processes, Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia. Available at http://www.kinetics.nsc.ru/kcp/mech.doc
- [29] A.A. Konnov, Detailed reaction mechanism for small hydrocarbons combustion. Release 0.5, (2000). Available as Electronic Supplementary Material to: F.H.V. Coppens, J. De Ruyck, and A.A. Konnov, The effects of composition on burning velocity and nitric oxide formation in laminar premixed flames of CH₄ + H₂ + O₂ + N₂, Combust. Flame 149 (2007), pp. 409–417.
- [30] A. Burcat, *Thermodynamic data*, Web site of the Laboratory for Chemical Kinetics, Institute of Chemistry, Eotvos University (ELTE), Budapest, Hungary. Accessed 14 August 2008 at http://garfield.chem.elte.hu/Burcat/burcat.html
- [31] R.J. Kee, F.M. Rupley, and J.A. Miller, Chemkin II: A Fortran chemical kinetics package for the analysis of gas-phase chemical kinetics, Report No. SAND89-8009, Sandia National Laboratories, 1989.
- [32] Y.B. Zeldovich, G.I. Barenblatt, V.B. Librovic, and G.M. Makhviladze, *The Mathematical Theory of Combustion and Explosion*, Consultants Bureau, New York, 1985.