

Chemistry of NO_x decomposition at flame temperatures

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Abstract

Detailed N/O kinetic sub-mechanism (for species containing only nitrogen and/or oxygen atoms) was updated on the basis of a literature survey of new experimental data for pertinent reactions. It was shown that without any adjustment of the rate constants the proposed N/O kinetic mechanism provides at least satisfactory agreement with different sets of experimental data on NO_x decomposition. Burning velocities of pure N₂O were measured at a pressure of 5 atm for further validation of the mechanism. It was found that the mechanism substantially underpredicts these data by a factor of approximately two. Possible reasons for this disagreement are suggested.

1. Introduction

Formation of nitrogen oxides (NO_x) and their reactions in flames are of major concern in many combustion systems. Ability to predict NO_x concentrations requires knowledge of detailed mechanism of pertinent chemical reactions. Investigation of nitrogen chemistry in combustion has already received much attention. However, in many cases there is still a lack of quantitative agreement between results of modelling and experimental data in respect of NO_x concentrations.

Reliable data for rate constants of N/O reactions are of great importance, because N/O kinetic sub-mechanism is a part of many combustion mechanisms. Previous version of detailed N/O kinetic sub-mechanism (27 reactions for 11 species) was proposed 10 years ago in 1999 [1]. Similar mechanism (23 reactions for 11 species including He) was proposed in 2000 in Ref. [2]. A review of elementary, homogeneous, gas phase reactions involved in combustion systems was published in 2005 [3]. In this review, rate constants for several hundreds reactions were evaluated. However, among these reactions there were only six reactions between species containing only N and/or O. Therefore the main goal of this work was to update N/O kinetic sub-mechanism and to validate it using literature data on NO_x decomposition at flame temperatures and new measurements of burning velocities of pure N₂O.

2. Reaction mechanism and its validation

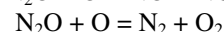
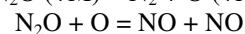
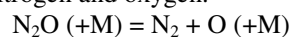
A literature survey was conducted to find new experimental data for pertinent reactions. The resulting mechanism consists of 29 reactions for 11 species (see Table 1). The previous version of the detailed N/O kinetic sub-mechanism [1] was extended by two more reactions. Rate constants of only 10 reactions remained the same. Uncertainties of the rate constants were evaluated. Thermodynamic data for N₂, NO₃ and N₂O₄ were updated according to recommendations of Burcat and Ruscic [4]. The present mechanism does not include

reactions of N₂O₅ radical, which should be taken into account in atmospheric pollutant chemistry.

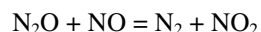
The Chemkin code [5] was used for the modelling. Experiments in static reactors were modelled as a constant volume adiabatic process or isothermal process for characteristic times longer than 10 seconds. Shock-tube measurements were modelled as constant pressure or constant volume adiabatic processes. Flames of nitrous oxide were calculated using the Premix code from the Chemkin Collection.

2.1. Nitrous oxide (N₂O)

Most important reactions in N₂O decomposition are reactions of nitrous oxide dissociation and its reactions with oxygen atom leading to formation of nitric oxide and molecular nitrogen and oxygen.



Also in some cases a reaction with nitric oxide can be important.



In the case of N₂O, experimental data on ignition delays and concentrations of O₂, NO and O were used for validation of the mechanism.

Ignition delays in mixture of 20% of N₂O with Ar were measured in reflected shock waves by Borisov and Skachkov [6] for pressures 2.5-3.5 atm and 10-14 atm. Shock tube data have been modelled at mean pressures of 3 and 12 atm, since the authors of [6] did not specify the pressure of individual experimental runs. Ignition delays were determined as times when rate of N₂O consumption reached its maximum value. Figure 1 shows that the modelling results are in good agreement with the experimental data for a pressure of 3 atm, but in the case of pressure of 12 atm the agreement is worse (the maximum difference is about 2 times).

Modelling results were also compared with experimental data on concentrations of NO [7, 8], O atom [9] and O₂ [10] during decomposition of N₂O.

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Table 1.

N/O kinetic mechanism: units are $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1} \text{cal}^{-1} \text{K}$, $k = AT^n \exp(-E_a/RT)$, UF = uncertainty factor

No.	Reaction	A	n	E_a	Temperatures	UF	Source
01.	$\text{O}+\text{O}+\text{M}=\text{O}_2+\text{M}^a$	1.00E+17	-1.0	0	300 - 5000	2	[19] ^c
	Enhanced third-body efficiencies (relative to Ar):						
	$\text{N}_2 = 2,$				2740 - 3460	1.6	[20]
	$\text{O} = 28.8, \text{O}_2 = 8, \text{NO} = 2, \text{N} = 2,$					2	[16], [21] ^c
	$\text{N}_2\text{O} = 4.38$						[22]
02.	$\text{N}_2+\text{M}=\text{N}+\text{N}+\text{M}^a$	1.00E+28	-3.33	225000	3390 - 6435	1.2	[23]
	Enhanced third-body efficiencies (relative to Ar):						
	$\text{N}_2 = 2.96, \text{O}_2 = 2.96, \text{NO} = 2.96, \text{N} = 6.6, \text{O} = 6.6$					2	[21] ^c
03.	$\text{N}_2+\text{O}=\text{NO}+\text{N}$	1.8E+14	0	76300	1700-4000	1.4	[3] ^c
04.	$\text{N}+\text{O}_2=\text{NO}+\text{O}$	5.85E+09	1.01	6200	300-5000	1.6	[24], [3] ^c
05.	$\text{NO}+\text{M}=\text{N}+\text{O}+\text{M}^a$	7.71E+19	-1.31	150000	2400-6200		[25], [26]
	Enhanced third-body efficiencies (relative to Ar):						
	$\text{NO} = 3,$						[25], [26]
	$\text{N}_2 = 1.5$						[27]
06.	$\text{NO}+\text{NO}=\text{N}_2+\text{O}_2$	3.0E+11	0	65000			[1]
07.	$\text{N}_2\text{O}(\text{+M})=\text{N}_2+\text{O}(\text{+M})^{a,b}$	9.9E+10	0	57900	1000-3000	3.2	[3] ^c
	Low pressure limit:	6.0E+14	0	57440	1000-3000	2.0	[3] ^c
	$F_{\text{cent}} = 1.167-1.25\text{e-}04 \text{ T}$				1000-3000	1.3	[3] ^c
	Enhanced third-body efficiencies (relative to Ar):						
	$\text{O}_2 = 1.4, \text{N}_2 = 1.7,$					1.4	[28]
	$\text{N}_2\text{O} = 3.5,$					2	[29]
	$\text{NO} = 3$					2	[21] ^c
08.	$\text{N}_2\text{O}+\text{O}=\text{N}_2+\text{O}_2$	3.69E+12	0	15940	1075-3340	1.6	[2], [3]
09.	$\text{N}_2\text{O}+\text{O}=\text{NO}+\text{NO}$	9.15E+13	0	27680	1370-4080	1.6	[2], [3]
10.	$\text{N}_2\text{O}+\text{N}=\text{N}_2+\text{NO}$	2.50E+12	0	20000			[30], [31]
11.	$\text{N}_2\text{O}+\text{NO}=\text{N}_2+\text{NO}_2$	2.75E+14	0	50000	1050-2500		[18]
12.	$\text{NO}+\text{O}(\text{+M})=\text{NO}_2(\text{+M})^{a,b}$	2.9E+14	-0.4	0	200-2200	2	[3] ^c
	Low pressure limit:	2.3E+20	-1.6	0	200-2200	2	[3] ^c
	$F_{\text{cent}} = 0.8$				200-2200	1.6	[3] ^c
	Enhanced third-body efficiencies (relative to Ar):						
	$\text{N}_2 = 1.46,$						[3] ^c
	$\text{O}_2=1.3, \text{NO} = 2.8, \text{NO}_2 = 10, \text{N}_2\text{O} = 7$					2	[21] ^c
13.	$\text{NO}_2+\text{O}=\text{NO}+\text{O}_2$	3.3E+12	0	-374	220-420		[32]
14.	$\text{NO}_2+\text{N}=\text{NO}+\text{NO}$	8.0E+11	0	-437	223-366		[33], [34], [35]
15.	$\text{NO}_2+\text{N}=\text{N}_2+\text{O}$	1.0E+12	0	-437	223-366		[33], [34], [35]
16.	$\text{NO}_2+\text{NO}=\text{N}_2\text{O}+\text{O}_2$	1.0E+12	0	60000			[36]
17.	$\text{NO}_2+\text{NO}_2=\text{NO}+\text{NO}+\text{O}_2$	3.95E+12	0	27590	473-2000	2	[1] ^c
18.	$\text{NO}_2+\text{NO}_2=\text{NO}_3+\text{NO}$	1.13E+04	2.58	22720	473-3000		[1] ^c
19.	$\text{NO}_2+\text{O}(\text{+M})=\text{NO}_3(\text{+M})^{a,b}$	3.5E+12	0.24	0	300-400	1.6	[37]
	Low pressure limit:	2.4E+20	-1.5	0	300-400	2	[37]
	$F_{\text{cent}} = 0.71*\exp(-\text{T}/1700)$				100-500		[37]
	Enhanced third-body efficiencies (relative to N_2):						
	$\text{Ar}=1.2$						[21] ^c
20.	$\text{NO}_3=\text{NO}+\text{O}_2$	2.5E+06	0	12120	298-934		[38]
21.	$\text{NO}_3+\text{O}=\text{NO}_2+\text{O}_2$	1.0E+13	0	0	297	2	[39]
22.	$\text{NO}_3+\text{NO}_2=\text{NO}+\text{NO}_2+\text{O}_2$	1.51E+10	0	2440	298-329		[40]
23.	$\text{NO}_3+\text{NO}_3=\text{NO}_2+\text{NO}_2+\text{O}_2$	5.1E+11	0	4870	298-329		[40]
24.	$\text{N}_2\text{O}_4(\text{+M})=\text{NO}_2+\text{NO}_2(\text{+M})^{a,b}$	1.15E+16	0	12840	250-300		[32] ^c
	Low pressure limit:	2.0E+28	-3.8	12720	300-500		[32] ^c
	$F_{\text{cent}} = 0.4$				300		[32] ^c
	Enhanced third-body efficiencies (relative to N_2):						
	$\text{Ar} = 0.8, \text{N}_2\text{O}_4 = 2, \text{NO}_2 = 2$					2	[21] ^c
25.	$\text{N}_2\text{O}_4+\text{O}=\text{N}_2\text{O}_3+\text{O}_2$	1.21E+12	0	0	199		[41]
26.	$\text{NO}_2+\text{NO}(\text{+M})=\text{N}_2\text{O}_3(\text{+M})^{a,b}$	1.6E+09	1.4	0	227-260		[42]
	Low pressure limit:	1.0E+33	-7.7	0	227-260		[42]
	$F_{\text{cent}} = 0.6$						[32] ^c

Enhanced third-body efficiencies (relative to Ar):

	$N_2 = 1.36$					[43]
27.	$N_2O_3 + O = NO_2 + NO_2$	$2.71E+11$	0	0	199	[41]
28.	$NO_2 + N = N_2 + O_2$	$2.4E+11$	0	-437	223-366	[33], [34], [35]
29.	$NO + NO + NO = N_2O + NO_2$	$1.07E+10$	0	26800	713-923	1.4 [39]

^a All other species have efficiencies equal to unity.

^b The fall-off behavior of this reaction is expressed in the form as used by Baulch et al. [3].

^c Review

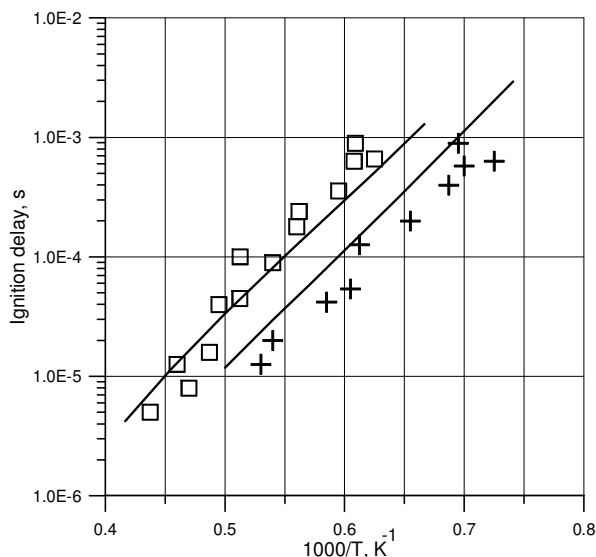


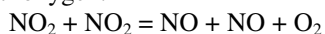
Fig. 1. Ignition delay in mixtures of 20% N_2O with Ar. Squares – 2.5-3.5 atm [6], crosses – 10-14 atm [6], lines – modelling.

In the last case a very good agreement was obtained between experimental and calculated data. In general, modelling results satisfactorily describes this set of experimental data for nitrous oxide decomposition – the maximal difference between them is ~ 2 times.

2.2. Nitrogen dioxide (NO_2)

To validate this branch of the mechanism experimental data on observed rate constants of NO_2 disappearance were used [11, 12]. Rosser and Wise conducted experiments in static reactors at temperatures lower than 1000 K [11]. The progress of decomposition was determined indirectly by observing the change in optical density with time of the reaction vessel content. Zuev and Starikovskii studied decomposition at higher temperatures using shock tube technique [12]. At low temperatures modelling results differ from experimental data by factor of 1.5 (see Fig. 2). Yet at higher temperatures the agreement is very good.

At low concentration of NO_2 and low temperatures, decomposition of nitrogen dioxide is determined only by one reaction, which leads to formation of nitric oxide and molecular oxygen.



At higher concentrations and temperatures, in addition to the above-mentioned reaction, other reactions also start to play an important role: another channel of $NO_2 + NO_2$ reaction leading to formation of

nitric oxide and NO_3 and also reactions of nitrogen dioxide dissociation and its reaction with oxygen atom.

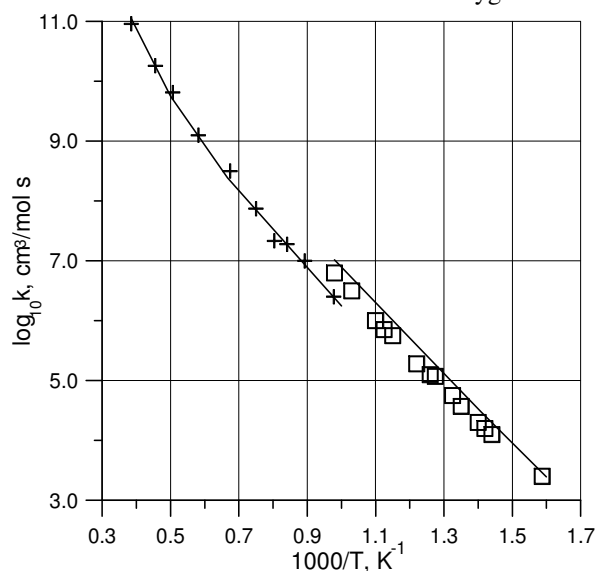
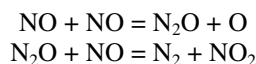


Fig. 2. Specific rate constants of NO_2 disappearance. Squares – $NO_2 (<1\%) - N_2$, $P < 1$ atm, $T = 630-1020$ K [11], crosses – 11.2 % $NO_2 - Ar$, $P \sim 1$ atm, $T = 1000-2630$ K [12], lines – modelling.

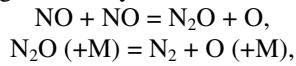
2.3. Nitric oxide (NO)

In the case of NO, experimental data on NO rate of disappearance and O atom formation rate were used for validation of the mechanism. Decomposition of 100% NO was studied at subatmospheric pressure by Kaufman and Kelso [13]. Modelling was conducted only in a temperature range of 1373-1533 K, because authors of [13] indicated that at lower temperatures the values of rate constants become questionable. Specific rate constants were determined at the moment when concentration of NO decreased by 1%. A good agreement was obtained between calculations and experimental data. The current mechanism gives values, which are higher than those measured in the experiment by a factor of 1.4 (see Fig. 3). The decomposition of nitric oxide in these conditions is determined mostly by 2 reactions.



The concentration of O atoms in the decomposition of nitric oxide has been monitored using atomic resonance absorption spectroscopy by Thielen and Roth [14] in a temperature range of 2380-3850 K at pressures 0.7-1.6 atm. Different mixtures were used: 0.1%-1% $NO - Ar$. Modelling results are also in a good

agreement with this set of experimental data. Formation of O atoms is governed by reactions:



with the former being the most sensitive.

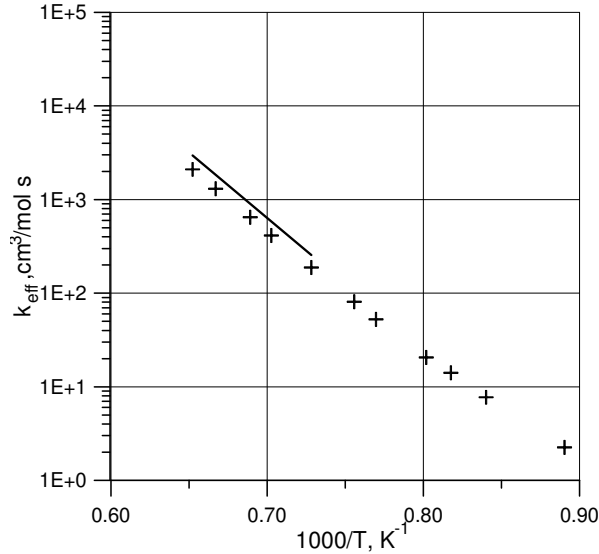


Fig. 3. Specific rate constant of NO disappearance. Crosses – 100% NO, P=0.65 atm [13], line – modelling.

2.4. Summary of the mechanism validation

Without any adjustment of the rate constants the proposed N/O kinetic mechanism allows at least satisfactory reproducing widely differing sets of experimental data on NO_x decomposition, obtained at initial concentrations of NO_x ranging from 0.1 to 100%, pressures ranging from 0.5 to 14 atm and temperatures ranging from 630 to 3850 K. Observed differences relate both to experimental uncertainty and uncertainty of our current knowledge of the rate constants of N/O reactions.

3. Experimental

It has already been known that a pure nitrous oxide can decompose in a self-sustained regime. However, experimental data on pure N₂O flame propagation were absent, most likely owing to a very slow rate of its decomposition. In this work the first attempt to measure burning velocities of pure N₂O was made. Experiments on laminar flame propagation in pure N₂O were performed at BAM in a high-pressure bomb (Fig. 4) at a pressure of 5 atm and initial temperatures of 25, 50, 100 and 200 °C. Ignition was centrally initiated by a spark and pressure-time-histories were measured.

For the calculations of the instantaneous burning velocity from the p(t)-history a spherical, thin flame front propagation in an adiabatic system was assumed. Burning velocity was calculated with two methods. One method, often used in safety studies, assumes a constant flame speed throughout the explosion. The second method, based on analysis of [15], allows for variable flame speed. In this approach, the flame radius was determined from the pressure record assuming an isentropic compression of the fresh gas as:

$$R_s(t) = R_b \left\{ 1 - \frac{p_{eq} - p(t)}{p_{eq} - p_o} \left(\frac{p_o}{p(t)} \right)^{1/\gamma} \right\}^{1/3}$$

where R_b is the equivalent radius of the combustion vessel, p_{eq} is the pressure at thermodynamic equilibrium at the end of constant volume combustion, p_o is the initial pressure and p(t) is the pressure at time t, γ is the specific heats ratio in the fresh gas, assumed constant. Then the mass burning velocity u_{nr} was calculated assuming that the combustion products are at the thermodynamic equilibrium:

$$u_{nr}(t) = \frac{1}{3} \cdot \frac{dp(t)}{dt} \cdot \frac{R_b^3 - R_s^3}{(p_{eq} - p(t))R_s^2}$$

This should be compared with the expression used in the first method:

$$S_n = \frac{\rho_u}{\rho_b} u_{nr} = \frac{R_b}{t} \cdot \left(\frac{p(t) - p_o}{p_E - p_o} \right)^{1/3} \cdot \left(1 + \frac{1}{\gamma} \frac{p_E - p_o}{p_o} \right)^{-2/3}$$

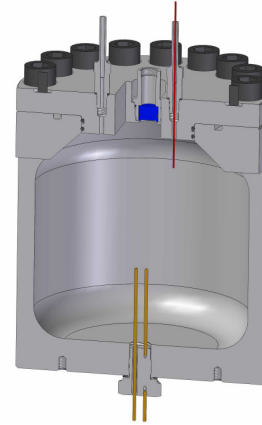
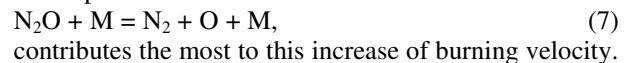


Fig. 4. A high-pressure bomb

4. Results and Discussion

Laminar burning velocities derived with both methods are shown in Figure 5. Crosses correspond to the first method and circles - to the second method. A good agreement between the results of the two different methods of experimental data processing was found. The difference between the modelling, shown as the solid line in Fig. 5, and experimental data, however, is quite large, and the burning velocity is systematically underpredicted. This calls for detailed analysis of possible uncertainties in the kinetic model.

Possible influence of the uncertainties of reaction rate constants on the model behaviour was analysed using the same brute force approach as in Ref. [16]. Uncertainties in third-body efficiencies were not taken into account in the present analysis. It was found that modification of the rate constants of all sensitive reactions to the limits of their uncertainty (without modification of the rate constant of reaction N₂O + NO = N₂ + NO₂) can increase the value of calculated burning velocity by ~70-75%. It should be noted that increase in the constant rate of reaction of nitrous oxide decomposition:



contributes the most to this increase of burning velocity.

However, it is not enough to approach the experimental data to the necessary degree.

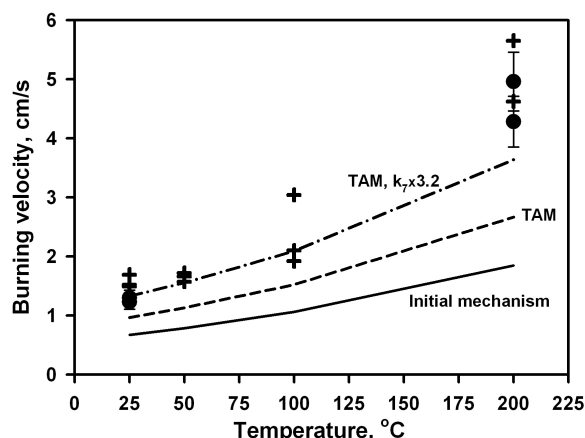


Fig. 5. Laminar burning velocities of pure N₂O at 5 atm as a function of initial temperature. Symbols: experiment, lines: modelling.

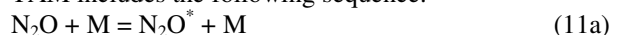
It means that special attention should be given to the reaction,



which has not been yet considered here. Burning velocity of pure N₂O is quite sensitive to this reaction. A reason for separate consideration of this reaction is based on findings of Zaslanko and Mukoseev [17]. They found an anomalous dependence of the rate constant of reaction (11) on concentration of NO in mixtures with N₂O and bath gas: the lower concentration of NO the higher the rate constant of this reaction. Moreover, the difference between highest and lowest values of the rate constant comprised 6-7 times. To explain their data Zaslanko and Mukoseev proposed so-called Thermal Activation Mechanism (TAM) [17]. Instead of a single reaction



TAM includes the following sequence:



The main idea behind this mechanism is that before a molecule (in this case N₂O molecule) can participate in the exchange reaction it should be collisionally activated.

To the best of our knowledge such an anomalous dependence for the rate constant of exchange reaction has not been reported by any other investigators, but it should be mentioned that the lowest value of the rate constant obtained in [17] (corresponding to the mixture 2.5% N₂O + 97.5% NO) is in a very good agreement with the rate constant of Borisov et al. [18], which is adopted in the current mechanism and is presented in Table 1. The rate constant proposed by Borisov et al. [18] for reaction between N₂O and NO is supported by a number of other investigations. Also in a way, it is supported by data of Zaslanko and Mukoseev. It was shown here that the mechanism with the rate constant of Borisov et al. reproduces, at least satisfactory, experimental data on N₂O decomposition, but fails to

predict burning velocities of pure N₂O (even after modification of rate constants of all other reactions within the limits of their uncertainty). Therefore we decided to incorporate the mechanism of thermal activation for reaction (11) in the mechanism with the rate constants: $k_{11a}=1.28\text{E}+11\exp(4600/\text{RT})$ and $k_{11b}=1.0\text{E}+13$. Results of calculations employing Thermal Activation Mechanism without modification of other rate constants are shown in Fig. 5 as dashed line. Calculated values are still lower than experimental data. Yet, implementation of TAM coupled with increase of the rate constant of reaction (7) within its uncertainty brings acceptable agreement with the experiment. These calculations are shown in Fig. 5 as dash-dot line. However, this increase of the rate constant of reaction (7) to its highest limit does not seem to be justified. It means that still a further analysis of both kinetic model and experimental data on N₂O burning velocities is required. It is perhaps appropriate to mention here that the flames in hand are slow and have a considerable thermal expansion, therefore the measured value of the flame speed can be affected by buoyancy distorting the flame shape. Another possible factor is that the high pressure flames often exhibit cellular structure resulting in faster burning; unfortunately, the combustion vessel does not provide means of the flame observation. Because of these factors, it is desirable to acquire more reliable experimental data on N₂O decomposition in order to establish the reasons of the disagreement between experimental and simulated data on N₂O burning velocities.

5. Conclusions

Updated N/O kinetic sub-mechanism at least satisfactory reproduces different sets of experimental data on NO_x decomposition. However, this mechanism failed to predict burning velocities of pure N₂O. It was shown that implementation of the mechanism of thermal activation for reaction N₂O + NO = N₂ + NO₂ provides better agreement with experimental data on burning velocities. However, it cannot fully compensate the observed difference between experimental and simulated data on N₂O burning velocities. Therefore, further analysis of both kinetic model and experimental data on N₂O burning velocities is needed.

References

- [1] A.A. Konnov, J. De Ruyck, Combust. Sci. Technol. 149 (1999) 53-78.
- [2] N.E. Meagher, W.R. Anderson, J. Phys. Chem. A 104 (2000) 6013-6031.
- [3] D.L. Baulch, C.T. Bowman, C.J. Cobos, R.A. Cox, Th. Just, J.A. Kerr, M.J. Pilling, D. Stocker, J. Troe, W. Tsang, R.W. Walker, J. Warnatz, J. Phys. Chem. Ref. Data, 34 (2005) 757-1397.
- [4] A. Burcat, B. Ruscic, "Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion with Updates from Active Thermochemical Tables" ANL-05/20 and TAE 960 Technion-IIT, Aerospace Engineering, and

- Argonne National Laboratory, Chemistry Division, September 2005.
<ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics>; accessed February 2008.
- [5] R.J. Kee, F.M. Rupley, J.A. Miller, M.E. Coltrin, J.F. Grcar, E. Meeks, H.K. Moffat, A.E. Lutz, G. Dixon-Lewis, M.D. Smooke, J. Warnatz, G.H. Evans, R.S. Larson, R.E. Mitchell, L.R. Petzold, W.C. Reynolds, M. Caracotsios, W.E. Stewart, P. Glarborg, C. Wang, O. Adigun, Chemkin Collection, Release 3.6, Reaction Design, Inc., San Diego, CA, 2000.
- [6] A.A. Borisov, G.I. Skachkov, *Kinetics and Catalysis* 13 (1972) 42-47.
- [7] J.P. Monat, R.K. Hanson, C.H. Kruger, *Combust. Sci. Technol.* 16 (1977) 21-28.
- [8] J.P. Monat, R.K. Hanson, C.H. Kruger, *Proc. Combust. Inst.* 17 (1979) 543-552.
- [9] S.K. Ross, J.W. Sutherland, S.-C. Kuo, R.B. Klemm, *J. Phys. Chem. A* 101 (1997) 1104-1116.
- [10] D.F. Davidson, M.D. DiRosa, A.Y. Chang, R.K. Hanson, in: K. Takayama (Ed.), *Shock Waves*, Vol. 2, Springer, Berlin, 1992, p. 8.
- [11] W.A. Rosser, H. Wise, *J. Chem. Phys.* 24 (1956) 493-494.
- [12] A.P. Zuev, A.Yu. Starikovskii, *Khim. Fiz.* 9 (1990) 1077-1088.
- [13] F. Kaufman, J.R. Kelso, *J. Chem. Phys.* 23 (1955) 1702-1707.
- [14] K. Thielen, P. Roth, *Proc. Combust. Inst.* 20 (1985) 685-693.
- [15] B. Lewis, G. von Elbe, *Flames, Combustion and Explosions in Gases*, 3rd Ed., Academic Press, London, 1987.
- [16] A.A. Konnov, *Combust. Flame* 152 (2008) 507-528.
- [17] I.S. Zaslanko, Yu.K. Mukoseev, *Khim. Fiz.*, 11 (1982) 1508-1517.
- [18] A.A. Borisov, G.I. Skachkov, A.A. Oguryaev, *Kinetics and Catalysis* 14 (1973) 294-300.
- [19] J. Warnatz, in: W.C. Gardiner, Jr. (Ed.), *Combustion Chemistry*, Springer-Verlag, New York, 1984, p.197.
- [20] S. Javoy, V. Naudet, S. Abid, C.E. Paillard, *Exp. Therm. Fluid Sci.* 27 (2003) 371-377.
- [21] O.E. Krivososova, S.A. Losev, V.P. Nalivaiko, Yu.K. Mukoseev, O.P. Shatalov, in: B.M. Smirnov (Ed.), *Plasma Chemistry*, vol. 14, Energoatomizdat, Moscow, 1987, p. 3.
- [22] J.J. Sangiovanni, T.J. Barber, S.A. Syed, *J. Prop. Power* 9 (1993) 134-138.
- [23] K. Thielen, P. Roth, *AIAA J.* 24 (1986) 1102-1105.
- [24] A. Fernandez, A. Goumri, A. Fontijn, *J. Phys. Chem. A* 102 (1998) 168-172.
- [25] K. Thielen, ARAS-Messungen zur Kinetik elementarer Hochtemperatur-Gasreaktionen von N-haltigen Molekülen. Dissertation, Universität Duisburg, 1988.
- [26] S. von Gersum, P. Roth, *Exp. Fluids* 13 (1992) 299-304.
- [27] W. Tsang, J.T. Herron, *J. Phys. Chem. Ref. Data.* 20 (1991) 609-663.
- [28] P. Glarborg, J.E. Johnsson, K. Dam-Johansen, *Combust. Flame* 99 (1994) 523-532.
- [29] W.D. Breshears, *J. Phys. Chem.* 99 (1995) 12529-12535.
- [30] R.K. Hanson, S. Salimian, in: W.C. Gardiner, Jr. (Ed.), *Combustion Chemistry*, Springer-Verlag, New York, 1984, p.361.
- [31] A. Fernandez, A. Fontijn, *Int. J. Chem. Kinet.* 33 (2001) 387-389.
- [32] R. Atkinson, D.L. Baulch, R.A. Cox, J.N. Crowley, R.F. Hampson, R.G. Hynes, M.E. Jenkin, M.J. Rossi, J. Troe, *Atmos. Chem. Phys.* 4, (2004) 1461-1738.
- [33] T. Nakayama, K. Takahashi, Y. Matsumi, K. Shibuya, *J. Phys. Chem. A* 109 (2005) 10897-10902.
- [34] P.O. Wennberg, J.G. Anderson, D.K. Weisenstein, *J. Geophys. Res.-Atmos.* 99 (1994) 18839-18846.
- [35] L.F. Phillips, H.I. Schiff, *J. Chem. Phys.* 42 (1965) 3171-3174.
- [36] C.F. Melius, in: S.N. Bulusu (Ed.), *Chemistry and Physics of Energetic Materials*, Kluwer Academic Publishers, the Netherlands, 1990, p. 51.
- [37] J. Hahn, K. Luther, J. Troe, *Phys. Chem. Chem. Phys.* 2 (2000) 5098-5104.
- [38] H.S. Johnston, C.A. Cantrell, J.G. Calvert, *J. Geophys. Res.-Atmos.* (1986) 5159-5172.
- [39] C.E. Canosa-Mas, P.J. Carpenter, R.P. Wayne, *J. Chem. Soc. Far. Trans. II* 85 (1989) 697-707.
- [40] R.A. Graham, H.S. Johnston, *J. Phys. Chem.* 82 (1978) 254-268.
- [41] R. Geers-Müller, F. Stuhl, *Chem. Phys. Lett.* 135 (1987) 263-268.
- [42] B. Markwalder, P. Gozel, H. van den Bergh, *J. Phys. Chem.* 97 (1993) 5260-5265.
- [43] I.W.M. Smith, G. Yarwood, *Farad. Discus. Chem. Soc.* (1987) 205-220.
- [44] A.A. Gvozdev, V.B. Nesterenko, G.V. Nichipor, V.P. Trubnikov, *Vestsi Akad. Navuk BSSR, Ser. Fiz.-Energ. Navuk* 2 (1979) 74-81.