On the detonation structure in ozone

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Introduction

Here we study the dynamics of detonation in gaseous ozone using a shock-fitting high order numerical method and several different kinetic mechanisms. The detailed mechanism of ozone decomposition is relatively simple consisting of three reversible reactions among O_3, O_2, and O. Hence this is one of the simplest real mixtures that can be relatively easily studied in terms of its detonation stability properties and nonlinear dynamics. In fact, one-dimensional detonation in ozone has recently been investigated by Aslam and Powers [1] using a high-order shock fitting method and a kinetic mechanism as given by Margolis [7] in his study of a laminar flame in ozone. The original data for the mechanism go back at least to the work of Hirschfelder et al [3]. There exist several other sources of kinetic data for ozone and here we investigate the extent to which these different data affect the structure of the steady detonation wave as well as its stability properties.

In addition to the kinetic parameters, accurate account for the thermodynamic properties will play an important role as well. Previously (e.g. [7]) the thermodynamics was treated in a simplified manner by assuming, in particular, the specific heats of different components to be the same and constant. In this paper, we relax this assumption and calculate all thermodynamic properties consistently as functions of temperature using the standard JANAF database.

Our ongoing work involves high resolution calculation of unsteady dynamics both in one and two dimensions with the focus on understanding the ozone detonation stability properties. The numerical algorithm used for this purpose is an extension of [10].

2 Governing equations and numerical algorithm

The governing equations are the standard reactive Euler equations for ideal-gas mixtures (e.g. [8]). We have integrated them using a modification of the algorithm of Henrick et al [2] that is fifth order

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	Reaction	$\log_{10} A$			β			$E, kcal/mole$		
1	$O_2 + M \Leftrightarrow O + O + M$	-17.023			2.5			117.27		
$1'$	$O + O + M \Leftrightarrow O_2 + M$		-30.480			-1			0	
2	$O_3 + M \Leftrightarrow O_2 + O + M$	-16.950	-7.1618		2.5	-0.589		24.12	23.2	
3	$O_3 + O \Leftrightarrow O_2 + O_2$	-17.119	-10.604	-13.509	2.5	-0.077	0.75	6.00	4.39	3.13

Table 1: Rate constants for ozone decomposition. Three sets are provided: the first column is from Margolis [7], the second from Magzumov [5, 6], and the third is the same as the first one with the exception of parameters for reaction 3, which are taken from Shaw [9].

accurate both in space and time. At each step of the Runge-Kutta time-integration, the rate equations (including the convective terms) were integrated from t^n to $t^n + \Delta t$ by Gear's method assuming constant temperature but variable concentrations.

The kinetic data for ozone decomposition that we use in this work are shown in Table 1. Several different sets of data have been used and detonation results compared against each other. The main difference among the sets is in the rate constants, not in the actual mechanism of ozone decomposition.

The species balance equations are

$$(\rho Y_i)_t + (\rho u Y_i)_x = \rho \omega_i, \quad i = 1, 2, ..., N,$$

where Y_i is the mass fraction of species i (and there are N species), ρ is the density, u is the flow velocity. The mass rate of production of species i is the sum over all J reactions in which the species may participate,

$$\omega_i = M_i \sum_{j=1}^{J} \nu_{ij} r_j, \quad i = 1, 2, ..., N, \tag{1}$$

where $\nu_{ij} = \nu'_{ij} - \nu''_{ij}$ is the difference of stoichiometric coefficients for the forward and backward reactions, respectively, M_i are the molecular weights, and the rate of reaction j is, by the law of mass action,

$$r_j = k_j^f \left[\prod_{k=1}^{N} c_k^{\nu'_{kj}} - \frac{1}{K_j^c} \prod_{k=1}^{N} c_k^{\nu''_{kj}} \right], \tag{2}$$

with the molar concentrations $c_k = \rho Y_k / M_k$ and equilibrium constants K_j^c. The forward rate constants are given by

$$k_j^f = A_j T^{\beta_j} \exp\left(-\frac{E_j}{RT} \right). \tag{3}$$

The parameters in Table 1 as well the values plotted in Fig. 1 correspond to this formula.

3 Discussion of the thermochemistry of ozone decomposition

We have tested various thermokinetic data for ozone decomposition. Figure 1 shows the rate constant for reaction 3, k_3^f, as a function of temperature in the range of temperatures from 300 K to 2000 K for various sets of data. We can see that most of the curves fall into a single cluster with the exception of two which have much larger values at high temperatures. The topmost curve corresponds to the data used by Margolis that have subsequently been used detonation studies [1]. Although the data are claimed to be the same as in Hirschfelder [3], we found that there is a significant difference in the temperature dependence of the pre-exponential factor (β_j in particular) between the two sets, which results in larger

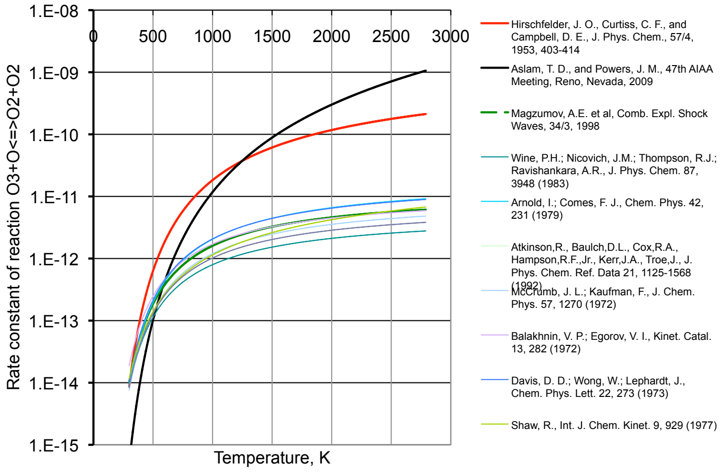

Figure 1: The dependence of the rate constant of reaction 3 on temperature for various mechanisms.

values of the rates for the Margolis' set. This in turn leads to significant reduction of the extent of the recombination zone and of the overall length of the reaction zone. At high temperatures that arise in detonations, especially during pulsations, this difference in the rates can lead to predictions that may be unrealistic. In particular, characteristic length scales may even end up outside of the domain of continuum approximation [1].

There are several factors that will play an important role in analyzing detonations in real mixtures. First of all, chemical rate constants are usually obtained in conditions (e.g. temperatures and pressures) which are far from those encountered in detonations. Consequently, any predictions we make about real detonations rest on a presumption that extrapolations of rate parameters into detonation states do not lead to significant differences. Furthermore, the accuracy of the kinetic data can be extremely poor even in the conditions in which they have been obtained. In the case of ozone detonation, we are currently using the data that have been obtained around 1930. They are hardly reliable enough for such sensitive predictions as detonation instability. As an example, the activation energy for $O_3 + O \to 2O_2$ that is taken to equal 6 $kcal/mole \cdot K$ in e.g. [1, 7] following the suggestion in Lewis and von Elbe's work in 1937 [4] (in fact, they make a reference to an even earlier work by Wulf in 1932 and Schumacher in 1930). Later studies, e.g. by Shaw [9], suggest using $E \approx 3\ kcal/mole \cdot K$ and this difference leads to significantly different predictions of detonation structure.

The second point that is important is the treatment of thermodynamic properties. The use of detailed chemistry loses much of its significance if thermodynamic properties are not calculated accurately. Although the approach based on simplified evaluation of heat capacities [7] still allows for some analysis of the role that the complex chemistry plays in detonations, the results so obtained may lead to qualitatively incorrect conclusions due to, for example, inaccurate predictions of the post-shock state and, consequently, of detonation stability properties.

4 The steady state structure and unsteady dynamics

Next we present the results (see Fig. 2) for the steady state structure with two mechanisms, by Margolis [3] and by Magzumov [5]. We have also included a modification of Margolis' data to a different set of parameters for $O_3 + O$ reaction that have been calculated by Shaw [9].

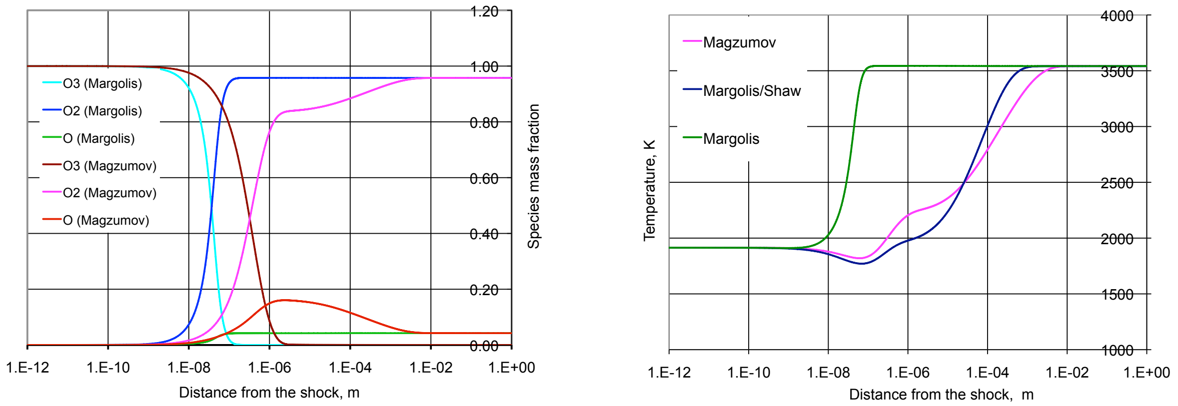

Figure 2: Left - profiles of the species mass fractions for two sets of data, by Margolis [7] and Magzumov [5]. Right - temperature profiles for the same two sets and the Margolis set modified by Shaw's data for $O_3 + O$ reaction. The detonation speed for these results was $D = 1940\ m/s$. Chapman-Jouguet speed for this mixture was calculated to be $D_{\text{CJ}} = 1906.4\ m/s$.

The most striking observation from these results is the difference in the extent of the recombination zones. While for the Margolis' set, the reaction is basically complete over the length of the order of $10^{-7}\ m$, the other sets predict that the reaction zone is much longer, by about four orders of magnitude. At the same time, the early stage of ozone decomposition is the same for all considered reactions and takes place over the length of about $10^{-8}\ m$.

The difference in the extent of the recombination zone between these chemical mechanisms must have dramatic consequences on the detonation stability properties. The natural expectation would be to anticipate instability in the case of Margolis' data due to a very rapid release of energy, effectively exhibiting a large-activation-energy behavior. Indeed, that is exactly what Aslam and Powers have found in their recent work [1], apparently based on a simplified treatment of thermodynamic properties of the mixture. Our calculations of the unsteady one-dimensional detonation in ozone indicates that with the rate parameters of Magzumov et al [5] as well as with other similar sets, the ozone detonation remains stable. Although we realize that much higher resolution simulations are needed to confirm these results beyond doubt, we note that the smallest grid size used in our present calculations was $\Delta x = 10^{-8}\ m$, that places one grid point on the early-stage plateau of the reaction when ozone starts decomposing into O_2 and O, while resolving the rest of the reaction zone very well. We believe that more accurate resolution of the early fine zone will not lead to any significant differences because this reaction proceeds essentially without any heat of reaction. The temperature is almost unchanged and the only role of this reaction is to start producing O_2 and O that subsequently react and release almost all of the energy. In [1], a similar choice of the grid size was made and pulsating instability was captured. We note that in [1], the extent of the plateau was on the order of $10^{-10}\ m$ which was also of the order of the smallest grid size used. Worse than in their case, however, the length scales for the chemistry we use spread over six orders of magnitude and performing well-resolved calculations becomes a difficult task. Nevertheless, such calculations are underway and we intend to include the results in a final version of the paper.

5 Conclusions

We investigated the structure of gaseous ozone detonation using variety of rate parameters for a three-step detailed chemical reaction mechanism that includes reactions among O_3, O_2, and O. We have found that the mechanism based on the parameter sets of Margolis [7] significantly overestimates the rates of the reaction $O_3 + O \Leftrightarrow 2O_2$ which leads to extremely fine length scales in detonation reaction zone that may not be realistic. Other rate data, in particular those of Magzumov et al [5], predict a very different structure of the reaction zone with significantly larger length scales. The rate data suggested in [11] also lead to results which agree closely with Magzumov's. We believe that this has qualitatively important implications for detonation stability. Our ongoing work explores this possibility by using resolved direct numerical simulations of the underlying reactive Euler equations.

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