Ignition Temperature vs Droplet Size for Hydrazine and Pentaborane in Air

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Theme

A NONLINEAR droplet ignition model (presented earlier[1,2]) incorporates finite-rate kinetics of arbitrary order and is distinguished from other models in that it exhibits a discontinuity at the ignition temperature. It is used here to show that for hydrazine and pentaborane, the required air temperature for ignition increases with decreasing droplet radius. Small droplets remain in the evaporative- or kinetic-controlled mode, while large droplets exist in the diffusion-controlled mode.

Content

In the mathematical model, a spherical, liquid fuel droplet is assumed to be in velocity equilibrium with its gaseous environment, while its interior is uniformly at its boiling point for the environmental pressure (1 atm herein). A pseudo-steady state prevails; the radius of the droplet (r_s) is held constant in an energy balance and fuel and oxidizer mass balances, which include chemical reaction at finite, temperature-dependent rates, radial convection of energy or fuel mass resulting from evaporation at the surface, and thermal diffusion from the environment or mass diffusion due to concentration gradients. Energy transport due to diffusive mass transfer, and mass diffusion due to the temperature gradient, are neglected. The model is limited by specification of a constant density and a Lewis number of unity. Using the method of Schvab and Zeldovitch to describe boundary conditions at the surface, expressions can be written for temperature, oxidizer concentration, and the dimensionless fuel mass burning rate, $a \equiv$ (burning velocity) (radius)/(diffusivity).

This system of equations constitutes a two-point boundary value problem for fuel mass fraction X_F, with **a** as an eigenvalue. For prescribed boundary conditions and physical properties of the fuel-oxidizer system, conditions at the droplet surface are computed for an assumed value of **a**, then a dimensionless fuel mass balance is integrated numerically outward from the droplet surface to some designated, large distance where an arbitrarily small X_F will be reached.

Calculations for hydrocarbon fuels[1,2] demonstrated that the curve for **a** vs environmental temperature T_∞ is S-shaped. Ignition due to diffusive heating is defined as the point where a discontinuity is observed in the mathematical model at the lower knee of the S-curve (i.e., two values of **a** both satisfy the boundary conditions). A second or reverse knee at lower T_∞ corresponds to the process of extinction. Diffusion-controlled combustion on the upper branch of the curve ceases, and a discrete decrease in **a** takes place, with a decrease in T_∞, at this point.

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The model incorporates a complete kinetic statement for a one-step chemical reaction whose order is stated in general terms, and a dimensionless reaction parameter includes both r_s and the chemical rate constant in an Arrhenius format. Thus, the contributions of r_s and chemical kinetics are coupled, and variations in estimates of Arrhenius constants (pre-exponential factor **A** and activation energy **E**) have effects equivalent to changes in r_s. First-order and second-order cases for hydrazine are examined; in each, the overall rate of oxidation is presumed to be controlled by a radical-forming hydrazine decomposition reaction (the reactions indicated in Fig. 1a). This view is in agreement with the observation[3a] that a small amount of oxygen does not accelerate the decomposition of hydrazine. For the first-order case, **A** and **E** were taken from Ref. 3b; for the second-order case, from Ref. 3c. Results for r_s vs T_∞ at ignition for these cases are presented in Fig. 1a.

For pentaborate oxidation, Price concluded that the reaction mechanism is of the branched chain type.[4] He hypothesized initiation reactions involving both pentaborate and oxygen and speculated that, at low oxygen concentrations, there is a reaction in the overall chain for which oxygen acts as an inhibitor. Snyder, Zanders and Skinner[5] found ignition induction time to be dependent of oxygen concentration and concluded that the first-order pyrolysis of pentaborate to two radicals is the controlling step in ignition; further, they observed an **E** for the pyrolysis that is within experimental error of that observed for oxidation. Their recommended values for **E** and **A** were 13.5 kcal/mole and $10^{5.6}$ sec^{-1}, respectively. Hairston[6] agreed on the first-order character of the pyrolysis reaction but reported 33.5 kcal/mole and 10^9 sec^{-1} for **E** and **A**, respectively. Chaney, Kibler, and Williamson[7] reported an **E** of 33.9 kcal/mole for pentaborate pyrolysis, over a substantial temperature range. Figure 1b shows results of our ignition calculations for the two values of **A** and various values of **E**. Again T_∞ at ignition increases with decreasing r_s.

For small droplets (large surface-area/volume ratio), evaporation is rapid, maintaining relatively low temperatures near the droplet; with large droplets, sufficiently higher temperatures arise to promote chemical reaction. For pentaborane this trend is consistent with general experience:

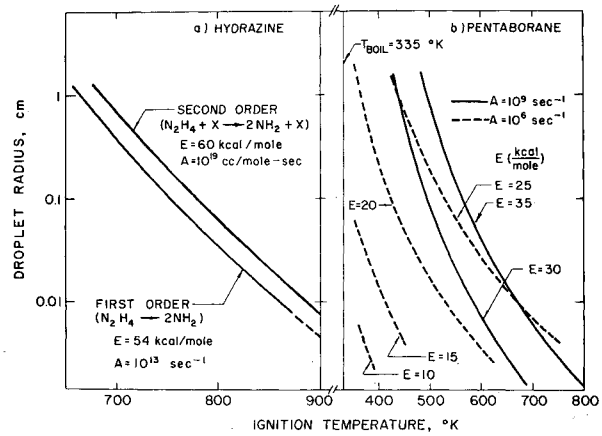

Fig. 1 Ignition temperatures for a) Hydrazine and b) Pentaborane droplets.

puddles, streams and large droplets ignite easily near room temperature, but fine sprays, aerosols, and vapor concentrations frequently fail to ignite.

References

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