Trioxane-Air Counterflow Diffusion Flames in Normal and Microgravity

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Introduction

Trioxane, a weakly bound polymer of formaldehyde (C₃H₆O₃, m.p. 61 °C, b.p. 115 °C), is a uniquely suited compound for studying material flammability. Like many of the more commonly used materials for such tests (e.g. delrin, polyethylene, acrylic sheet, wood, and paper), it displays relevant phenomena (internal heat conduction, melting, vaporization, thermal decomposition, and gas phase reaction of the decomposition products). Unlike the other materials, however, it is non-sooting and has simple and well-known chemical kinetic pathways for its combustion. Hence it should prove to be much more useful for numerical modeling of surface combustion than the complex fuels typically used.

We have performed the first exploratory tests of trioxane combustion in the counterflow configuration to determine its potential as a surrogate solid fuel which allows detailed modeling. The experiments were performed in the spring and summer of 1998 at the National Institute of Standards and Technology in Gaithersburg, MD, and at NASA-GRC in Cleveland. Using counterflow flames at 1-g, we measured the fuel consumption rate and the extinction conditions with added N₂ in the air; at μg conditions, we observed the ignition characteristics and flame shape from video images. We have performed numerical calculations of the flame structure, but these are not described here due to space limitations. This paper summarizes some burning characteristics of trioxane relevant to its use for studying flame spread and fire suppression.

Experiment

A stagnation flow of air (with optional N₂ diluent) against a horizontal, planar surface of trioxane was used to establish a counterflow diffusion flame. The oxidizer was supplied from above via a stainless steel jet (2.27 cm I.D. with three 60 mesh/cm screens to provide uniform laminar flow), which was located 1 cm above the trioxane, while a concentric stainless steel tube (5.35 cm I.D.) provided a co-flow of nitrogen [1]. The trioxane was supplied in two separate ways. In the first, a small puck of solid trioxane was formed in the counter-bored region of an aluminum alloy plate (56 mm x 78 mm, 6.28 mm thick, with a 24.1 mm diameter, 3.1 mm deep hole in the center). The trioxane was melted and poured into the hole, overfilling it by about 1 mm, and allowed to solidify at the laboratory temperature (21.0 ± 1.5) °C. The airflow was set to the desired value, and the flame was established, causing the trioxane to melt, vaporize, and burn. The fuel surface regressed during the test, but data were only used for trioxane levels within ±1.5 mm of the edge of the Al plate. To obtain the fuel consumption rate, the Al plate and trioxane puck were positioned on a scale (Mettler², model PE360), and the weight as a function of time was recorded by a computer.

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² Certain commercial equipment, instruments, or materials are identified in this paper to adequately specify the procedure. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment are necessarily the best available for the intended use.
In the second apparatus, a high-pressure syringe pump (Isco, model 314, insulated and heated to (70 ±5 °C) injected liquid trioxane continuously [2] to a small pool (formed by a 2.54 cm O.D. stainless steel tube with 1.64 mm walls, and 12 mm deep). The transfer lines and fuel cup were held at (100 ± 5 ) °C. A concentric stainless steel tube (47.8 cm I.D.) filled with glass beads allowed for co-flowing N₂ gas. The trioxane level was held flush with the top of the fuel cup through manual control of the piston pump rate (which varied with the strain rate and N₂ mole fraction). The global strain rate in the flame is estimated using the formulation of Seshadri and Williams [3] as 2V_{air} / L. Here, V_{air} is the gas exit velocity from the air jet, and L is the spacing between the air jet exit nozzle and the fuel surface.

Gas flows were measured with digitally-controlled mass flow controllers (Sierra Model 860) with a quoted repeatability of 0.2% and accuracy of 1% of full-scale flow, which were calibrated with bubble (Gillian Gilibrator) and dry (American Meter Co. DTM-200A) flow meters so that their accuracy was 2% of the indicated flow. House compressed air (filtered and dried) was used after it was additionally cleaned by passing it through an 0.01 μm filter, a carbon filter, and a desiccant bed to remove small aerosols, organic vapors, and water vapor. The 1,3,5 trioxane was from Aldrich (99+%), and the added nitrogen was boil-off from liquid N₂.

All uncertainties are reported as expanded uncertainties: X ± U, where U is kuc, and is determined from a combined standard uncertainty (estimated standard deviation) uc, and a coverage factor k = 2 (level of confidence approximately 95%) [4]. Likewise, when reported, the relative uncertainty is U / X · 100%, or kuc / X · 100%. The expanded relative uncertainties for the experimentally determined quantities in this study are indicated on the figures.

Exploratory tests of the behavior of trioxane-air flames in μg were conducted in the GRC 2.2-second drop tower. The multi-purpose combustion rig was used. Melted trioxane was poured into a counter-bored region of a 51 mm x 51 mm x 6.4 mm thick Teflon holder and allowed to solidify and reach laboratory temperature. The recessed trioxane sample in the holder was 25.4 mm in diameter 3.2 mm thick; however, the trioxane was typically overfilled by about 1 mm. The Teflon fuel holder was screwed to an aluminum standoff 50 mm above the base of the combustion chamber. Provisions were made for supplying ambient air from a 12.2 mm diameter nozzle located 21 mm from the sample surface, so the flame could be tested with and without imposed flow. The trioxane was ignited with a 6 cm length of 0.255 mm diameter Kanthal wire just touching the trioxane surface. Video images were obtained with a fiber-coupled camera.

**Results and Discussion**

For strains above 100 s⁻¹, the counterflow trioxane flames were bright blue and non-sooting, and planar and parallel to the fuel surface. As the strain decreased, or the added N₂ was increased, the intensity of the blue flame emission decreased, but the color was unchanged. We could not extinguish flames of trioxane and pure air by increasing the air flow since for those conditions, the strong air jet (strain > 1000 s⁻¹) blew the liquid trioxane out of the fuel cup. Flames in 1-g supported by natural convection were also stable.

Figure 1 shows the trioxane fuel consumption rate for both burners (solid puck of trioxane and the liquid feed system). Both indicate an approximately linear relationship between strain (i.e. imposed air velocity) and fuel consumption rate, with a fuel consumption rate of about 0.5
g/cm²/min at a=300 s⁻¹. It is somewhat surprising that the two different techniques show approximately the same fuel consumption rate. It is likely that the puck method is influenced by transient thermal effects, while the liquid feed system would require careful balancing of the heat flows for accurate measurement of fuel consumption rate. Great pains were not taken in these preliminary tests to account for or control either of these influences.

The effect of nitrogen added to the air stream on the fuel consumption rate is shown in Figure 2. Data are presented for 0, 10, 20, 30, and 40% added nitrogen mole fraction in air. To first order, the effect of added nitrogen is approximately linear, with nitrogen addition decreasing the fuel consumption rate proportionately. The extinction condition of the continuous feed trioxane burner with added N₂ is shown in Figure 3. The mole fraction of added N₂ required for extinction decreases from 41% at a strain of 150 s⁻¹ to 25% at a=550 s⁻¹. A linear extrapolation implies an extinction condition of 48% added N₂ at zero strain, and an extinction strain rate of 1100 s⁻¹ with pure air.

Trioxane-air flames in the drop-rig (trioxane puck in a Teflon holder) are shown in Figure 4. The top image is in 1-g, with no imposed flow. The second through fourth images are all in μg, with increasing imposed flows of 0, 640, and 1100 sccm. All fuel reservoirs are 25.4 mm in diameter except the bottom one, which is 22.2 mm. Remnants of the igniter wire are visible in each image for the μg flames.

Conclusions

Trioxane is an easy fuel to work with for combustion studies of material flammability. Flames can be established over a wide range of strain rate and oxygen mole fraction in the air, in both normal and microgravity. Trioxane is easily ignited in μg, and the flame is stable in both 1-g and μg with no imposed flow. The intensity of the flame emission (and presumably the temperature and heat release rate) increases as the imposed airflow increases. The fuel consumption rate and the intensity of visible flame emission are amenable to straightforward laboratory experiments. The kinetic studies (not discussed in the present work) show the decomposition pathway of trioxane to be simple, proceeding through CH₂O→HCO→CO→CO₂ mostly via H-atom attack on CH₂O, thermal decomposition of HCO, and OH attack on CO. With trioxane, it should be possible in models of material flammability to include realistic fuel decomposition kinetics to describe the gas-phase chemistry. Since we are interested in studying the effect of physical and chemical inhibitors on condensed-phase flames in microgravity, trioxane may be a useful fuel for this purpose.

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References

Figure 1 – Trioxane consumption rate vs. strain; puck and and continuous feed systems.

Figure 2 – Trioxane consumption vs. strain in liquid system at 0, 10, 20, 30, and 40% added N₂ in air.

Figure 3 – Mole fraction of added N₂ in air vs. extinction strain rate for liquid trioxane burner.

Figure 4 – Video images of trioxane-air flames. Top image is in 1-g with no imposed flow. The second through fourth from the top are in μg, with imposed flows of 0, 640, and 1100 sccm.