



Application of molecular beam mass spectrometry in studying the structure of a diffusive counterflow flame of CH_4/N_2 and O_2/N_2 doped with trimethylphosphate

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Abstract

The applicability of molecular beam mass spectrometry (MBMS) in studying the structure of counterflow flames has been tested by investigating a counterflow flame of CH_4/N_2 and O_2/N_2 . The thermal structure of the flame was examined using a microthermocouple; the concentration profiles of such stable species as CH_4 , O_2 , and CO_2 were measured by sampling with a microprobe and MBMS at various positions. The microprobe did not disturb the flame. However, the sonic probe, when inserted into the flame transverse to the burner axis to measure the centerline concentration profiles, produced a significant disturbance of the flame. But no such disturbance was observed when the tip of the sonic probe was located at the periphery of the burner. Good agreement was obtained between the concentration profiles of stable species, as measured using a microprobe and a sonic probe at the periphery of the burner. To verify the applicability of MBMS for detecting radicals and other labile species in a counterflow flame, the concentration profiles of H, OH, and the main phosphorus-bearing species in the counterflow flame doped with trimethylphosphate (TMP) were measured by MBMS at the periphery of the burner and compared with results of modeling using the OPPDIF code and a mechanism for the combustion of TMP, tested previously in premixed flames of methane and oxygen with TMP as an additive. Good agreement was obtained between the measured and simulated concentration profiles for the reagents, as well as for the final and intermediate products with relatively high molecular weights (PO , PO_2 , HOPO , HOPO_2). The measured concentration profiles of species with low molecular weights (H_2O , CO_2 , OH , H) were found to be broader than the calculated ones—in fact, the lower the molecular weight, the wider was the profile. This is probably due to a real flame not being one-dimensional.

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1. Introduction

Molecular beam mass spectrometry (MBMS) is one of the most effective techniques for studying the chemical structure of a flame. It allows one to iden-

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tify both stable and labile species, including atoms and free radicals, as well as to measure their concentrations and their spatial distributions. A comparison of experimental results with modeling of the structure of a flame provides information on the mechanisms and kinetics of the major chemical reactions occurring. Although MBMS has been widely used to explore the chemical structure of flames stabilized on a flat burner, there have been no MBMS studies of the structure of counterflow diffusion flames, which have recently become a subject of increased interest. In previous studies e.g., [1–5], the structure of counterflow flames has been studied by sampling with a quartz microprobe with a subsequent chromatographic analysis of the sample. A major advantage of sampling with a microprobe is the negligible thermal and gas-dynamic perturbations of the flame induced by a microprobe. Quenching a chemical reaction in the sample and thus the measurements of concentration profiles are known to depend significantly on such parameters of the probe as its internal angle, the diameter of the orifice, and the nature of its internal surface, because heterogeneous reactions do take place on the hot inner walls of the microprobe. Consequently, with a microprobe, labile species (atoms, radicals), as well as many stable species, can decompose or react on the inner walls of the microprobe as well as in the gas phase. In the above papers as well as in many other works, only the size of the orifice ($\sim 0.06\text{--}0.5$ mm) and the diameter ($\sim 0.1\text{--}1$ mm) of the outer tip were specified. However, the value of the internal angle does not allow one to estimate the quality of the measurements. Of course, the internal angle of the cone characterizes the sample's freezing. Gas-phase chemical reactions are known [6] to occur in probes with too wide an internal angle. Height et al. [7] attached an alumina capillary to an alumina tube (O.D. 1.6 mm) as a probe for studying the structure of counterflow natural gas/air flames. Choking in the probe should be experimentally verified by measuring flow rates of postflame gases through the microprobe, while varying the back pressure in the sampling system, similarly to [8,9]. However, in most works, this testing was not carried out. We conclude that using capillaries or microprobes with small cone angles for gas sampling can cause errors in measurements of concentrations in a flame.

A diffusive counterflow flame of CH_4/N_2 and O_2/N_2 doped with trimethylphosphate (TMP) is very appropriate for verifying the applicability of MBMS, which has been extensively used to study the structure of premixed flames doped with organophosphorus compounds (OPCs) [10–24]. It has been shown that the phosphorus oxides catalyze the recombination of the radicals H, O, and OH [15–17] and so play a key role in flame inhibition by OPCs. Several de-

tailed reaction mechanisms for OPCs, including TMP, have been developed previously [10,19,25–28], but there are still significant gaps and uncertainties in the inhibition mechanism. In addition, there are discrepancies between experiments and simulations. To improve existing kinetic models, one needs a wide range of measurements of the structure and burning velocity of premixed and diffusion flames. One gap is in experiments on the structure of counterflow flames with OPCs as additives. Laser-induced fluorescence (LIF) has been used to measure concentration profiles for OH radicals in counterflow flames doped with OPCs [10,12,13,29,30]. However, it is especially necessary to also have experimental profiles of both stable and labile species, such as the hydrogen atom, PO and PO_2 radicals, and other P-bearing species, such as HOPO, HOPO_2 , and $\text{PO}(\text{OH})_3$. The latter cannot be detected by microprobe sampling techniques or LIF. MBMS studies of the structure of counterflow flames doped with OPCs have not been reported until now. This study is of a counterflow diffusion flame of CH_4/N_2 and O_2/N_2 without an additive and with TMP added to the oxidizer flow. The goal of this work was to verify the applicability of MBMS in determining the structure of counterflow flames. In addition, this MBMS study aims to validate a previously developed mechanism of flame inhibition by OPCs by comparing measurements with the results of simulations of flame structure.

2. Experimental details

A counterflow diffusion flame of CH_4/N_2 (0.2/0.8) and O_2/N_2 (0.4/0.6) was stabilized on an opposed-jet burner at atmospheric pressure (755 ± 5 Torr). Fig. 1 shows the burner. The reactants passed through nozzles, which were straight quartz tubes; flowing nitrogen was used as a sheath. The volumetric flow rates for the streams of fuel and oxidizer under ambient conditions were both 20 ml/s and were set with an

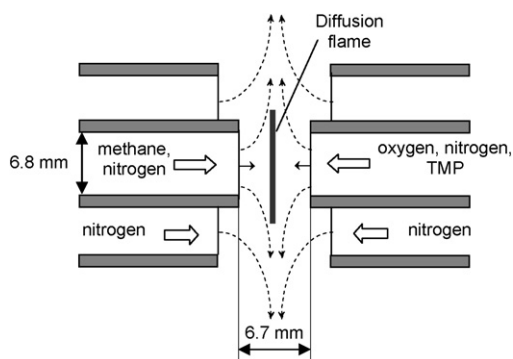


Fig. 1. Counterflow burner.

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