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MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

SIXTEENTH QUARTERLY TECHNICAL SUMMARY REPORT
1 July - 30 September 1965

Contract No. Nonr-5599(00)
ARPA Order No. 23-63, Amendment No. 38
Program Code No. 4910

MRI Project No. 2551-P

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by

Thomas A. Milne

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PREFACE

This report was prepared for the Advanced Research Projects Agency under ONR Contract No. Nonr-3599(00), monitored by Mr. Roland Jackel and Dr. Ralph Roberts of the Power Branch, ONR.

The report describes attempts to see Si and Ti species in various flames, the effect of orifice shape on beam formation and flame stability, and some results of probing the reaction zone of low pressure flames.

The research was conducted by Dr. Thomas A. Milne, project leader, Dr. Frank T. Greene and Mr. Jacob Beachey. Mr. Gordon Gross has contributed greatly through discussions and reviews of the work.

Approved for:

MIDWEST RESEARCH INSTITUTE



Sheldon L. Levy, Director
Mathematics and Physics Division

11 November 1965

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SUMMARY

Cyanogen-oxygen flames have been sampled at one atmosphere at temperatures such that the O_2 and CO_2 are largely dissociated. Addition of $TiCl_4$ to such flames has allowed the observation of TiO^+ and Cl^+ but under conditions which suggest that they arise largely from $TiOCl(g)$ transpired from the oxide deposited on the cold probe. A study of beam formation from cones with apex angles from 90 degrees to 30 degrees was made. Serious intensity attenuation was observed with angles sharper than 60 degrees. Sharp-edged, 90 degrees, cooled, stainless steel cones, 1/2-in. long, produced strong beams, and it was possible to probe the reaction zones of lean, CH_4-O_2 , 1/20 atmosphere flames without serious disturbance. Preliminary profiles through such flames, with and without CH_3Br inhibitor, are discussed.

I. INTRODUCTION

The failure so far to quantitatively sample, with cold orifices, easily condensable species from hot flames has led us to a crucial point in the course of this program. If flame-orifice interactions lead to inherent complications in using cold probes then the best route to new thermo-chemical data would appear to be through the use of isothermal studies (in which the orifice is in thermal equilibrium with the flame) over a more restricted temperature range but extending to much higher pressures than has been possible in previous mass spectrometric work. If, on the other hand, condensation or nucleation effects, inherent in the expansion of the gas into a molecular beam, are the real problem, then these phenomena should be studied to allow evaluation of this problem and its implications in a variety of experimental situations.

In the following sections are described the past quarter's efforts to define the controlling problem and to determine the best direction for continuing work.

II. OBSERVATION OF METAL-CONTAINING SPECIES IN FLAMES

In order to make conditions as favorable as possible for sampling refractory species from flames, we have employed hotter flames than have been used previously.^{1/} The hotter flame not only maintains the tip of the sampling orifice at a higher temperature but also results in the metal-containing species being further from saturation as sampling begins. Cyanogen-oxygen flames varying from stoichiometric to lean have been burnt at one atmosphere on small, uncooled, glass-blowing torch tips.

The sampling orifice consisted of a 1/8 in. high, 90 degree cone, spun from 0.005 in. thick Pt-Rh sheet with a 0.008 in. diameter hole drilled in the apex. This water-cooled orifice reached white heat in these flames but did not sag. Stable products and free radicals were sampled from several flames as a preliminary check before adding metals. Sampling was from a region about 1 mm. above the inner cone of the C₂N₂-O₂ flames burning on a 1 mm. diameter torch tip.

Table I shows the results obtained in several experiments. Note the high degree of dissociation of both O₂ and CO₂ in the hotter flames. From these data one can obtain an indication of temperature by calculating such equilibria as $O_2 \rightarrow 2O$, $CO + O \rightarrow CO_2$ and $N_2 + O_2 \rightarrow 2NO$ and comparing them

with thermochemical data. In this way the 50-50 flame $\text{CO} + \text{O} \rightarrow \text{CO}_2$ equilibrium corresponds to about $3750^\circ\text{K} \pm 200$ while the 34-66 flame equilibria $\text{O}_2 \rightarrow 2\text{O}$, $\text{CO} + 1/2 \text{O}_2 \rightarrow \text{CO}_2$ and $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$ all correspond to a temperature of $3150^\circ\text{K} \pm 200$.

TABLE I

SPECIES OBSERVED BY DIRECT SAMPLING OF THE BURNT GAS REGION OF $\text{C}_2\text{N}_2\text{-O}_2$
FLAMES BURNING AT ONE ATMOSPHERE ON SMALL TORCH TIPS
 (The flames are listed in order of decreasing temperature.)

Flame Composition (%)		Electron Energy (ev.)	16 ⁺	28 ⁺	30 ⁺	32 ⁺	44 ⁺
<u>C₂N₂</u>	<u>O₂</u>						
50	50	20	15	-	-	< 15	-
45	55	20	40	1,100	-	25	< 25
40	60	20	60	-	-	25	75
34	66	20	65	-	-	100	275
50	50	50	5,000	96,000	-	< 250	460
34	66	50	-	120,000	6,200	6,600	11,000

In using the above procedure one makes the as yet unproven assumption that combustion was complete at the region in the flame where sampling occurred. The main points we are making are: (a) that these flames are very hot, (b) that such hot flames could be studied in detail mass spectrometrically, and (c) in our Si and Ti experiments the gaseous oxides should be initially far removed from saturation.

The 34-66 flame was used for sampling studies with SiCl_4 and TiCl_4 additives. The expected equilibrium species are $\text{SiO}(\text{g})$ and $\text{TiO}_2(\text{g})$, respectively. A search was made for such species coming directly from these flames and the results were negative. However, the following observations were made. The species SiO^+ and TiO^+ , together with Cl^+ , were observed in the mass spectrum under certain circumstances. With these hot flames, the oxide that builds up on the tip of the orifice is quite hot. A short while after adding SiCl_4 or TiCl_4 to the flames the species SiO^+ and TiO^+ appeared but did not disappear when the additive was turned off and the flame left on. This suggests quite strongly that material was being removed from the oxide layer and swept into the supersonic beam. Since Cl^+ was observed also it is quite possible that a more volatile oxychloride of Si and Ti deposited on the orifice and continued to vaporize in the hot flame gases. The gradual unplugging

of partially plugged orifices which occurred under these circumstances is consistent with this picture.

There are a number of implications of this explanation. On the positive side, the species giving rise to SiO^+ and TiO^+ did survive the expansion to a beam, thus indicating that nucleation did not completely dominate the picture. On the negative side, the fact that material on the walls near the orifice entrance can get into the centerline flow leading to the observed molecular beam is disturbing and clearly indicates, for this experimental case at least, that an ideal expansion upstream of the orifice is not being obtained. As a practical matter such side effects constitute one more handicap in sampling condensible species with cold orifices.

With regard to minimizing cold-orifice perturbations of the sampled gases we see only one remaining parameter to be studied -- the angle and sharpness of the orifice. It appears that with the 90 degree spun orifices used in the past there was appreciable turbulence in the immediate vicinity of the hole. We will test very sharp-edged cones (fabricated from foil by spot-welding) with Si or Ti additives. It may also be possible to design a contoured cone which gives an appropriate turning angle and still does not disturb the centerline flow of a free jet expansion. If the previously noted complications are not alleviated, then our full attention will go to isothermal studies and to nucleation of high temperature species.

III. ORIFICE CONFIGURATION EFFECTS

In preparation for sampling of metal species with sharper orifices and in connection with studying the reaction zones of low pressure flames, we have measured beam intensities and flame perturbations with cones sharper than 90 degrees. The qualitative results can be summarized as follows. Cones of 90 degrees or less and of length 1/2 in. or more appear to penetrate 1/20 atmosphere $\text{CH}_4\text{-O}_2$ flame reaction zones without visible perturbation. Some profiles are shown in a later section. Beam intensities do vary markedly with cone angle, however. In general, 60-degree cones give beams about an order of magnitude less intense than 90-degree cones and intensities from 45-degree and 30-degree cones are too low to be useful. The reduction in intensity with sharper cone angle is more serious at lower pressures. Sherman^{2/} indicates the fluid mechanical effects which may account for these observations. We are using 90-degree cones in current flame work, but of greater length and with sharper inlet geometry than the previously used spun cones.

IV. ISOTHERMAL EXPERIMENTS

A heated-orifice sampling device has been constructed for use with low temperature flames or other sources. It is constructed of stainless steel and suitable for about 1200°K. This inlet system will allow the orifice to be kept at the same temperature as the flame gases, or cooler, as desired. The initial test will be with the species $\text{HBO}_2(\text{g})$ in a $\text{H}_2\text{-O}_2\text{-N}_2$ flame. We expect also to generate the $\text{HBO}_2(\text{g})$ by bubbling steam through furnace-heated molten B_2O_3 . The latter apparatus, substituting for a flame, would also serve for the study of nucleation and thermodynamics in other chemical systems such as salts, refractory metal oxide-water systems, etc.

These isothermal experiments should convincingly isolate the source of the problem in cold orifice flame sampling.

V. REACTION ZONE PROFILES IN LOW PRESSURE FLAMES

In connection with internally sponsored work on the direct sampling of reaction zones of low pressure flames, results of interest to this project were obtained using the molecular beam inlet system. The orifice was a spot-welded, 1/2 in. long, 90-degree, sharp-edged cone containing a 0.010 in. diameter hole. It was made by folding 0.002 in. thick stainless steel sheet. Profiles were taken through a flame close to the composition previously studied by Wilson^{4/} (who used techniques worked out by Fristrom and Westenberg). Figure 1 shows profiles of species in a 1/20 atmosphere lean $\text{CH}_4\text{-O}_2$ flame. The ion intensities are expressed in arbitrary units and have not been corrected for mass spectrometer sensitivity or mass separation effects. A comparison with Wilson's^{4/} profiles shows a very close correspondence in the relative changes in concentration with distance. Our next test will be to try to determine the OH and O profiles in this flame, OH having already been quantitatively sampled in the burnt gases.

As a further test we added about 1 per cent CH_3Br to the Wilson flame and were able to follow the destruction of CH_3Br , the early appearance and later destruction of HBr and the gradual conversion of the bromine to Br atoms. These first CH_3Br experiments presented some difficulty and mass balances were not too good; nevertheless, the ability to follow Br and HBr was demonstrated and indications are that Wilson's HBr concentrations are a factor of 5 - 10 low.

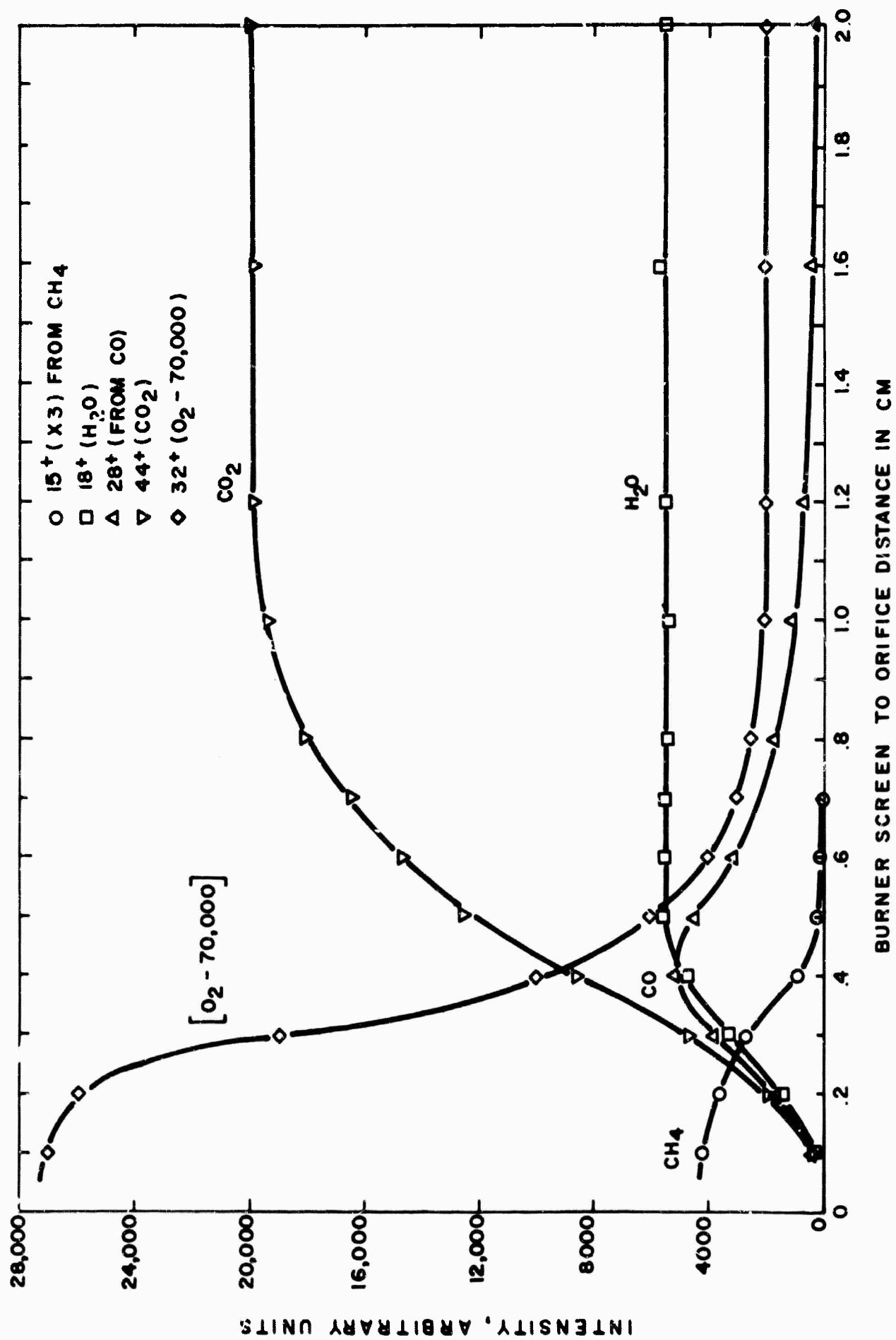


Fig. 1 - Species Profiles Taken by Direct Sampling Through a Lean, 1/20 Atmosphere CH₄-O₂ Flame

VI. FUTURE WORK

The following experiments will be performed as soon as possible to determine the major direction of future effort:

1. The detection of Si-O or Ti-O species and the plugging behavior in various flames using cold, sharp-edged, 90-degree orifices.

2. The study of the species $\text{HBO}_2(\text{g})$ sampled in an isothermal experiment and then with progressively cooler orifices. We will then pursue a program of equilibrium and/or nucleation studies on systems involving metals, oxygen and water either in flames, if cold orifice effects can be overcome, or with other heat sources in isothermal situations.

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