Thermochimica Acta, 8 (1974) 363–367

OXYGEN AND HYDROGEN ATOM CONCENTRATION PROFILES IN THE PREMIXED PROPANE/OXYGEN FLAME

W. R. DOWNS AND E. L. SIMMONS*
Structures and Mechanics Division, National Aeronautics and Space Administration,
Lyndon B. Johnson Space Center, Houston, Texas 77058 (U.S.A.)

(Received 27 September 1973)

ABSTRACT

The oxygen and hydrogen free radical (atom) concentration profiles in the premixed propane/oxygen flame at 92.5% oxygen were determined using electron spin resonance (ESR) spectroscopy techniques. The ESR instrument was specially modified so that the flame can be probed for determining the oxygen and hydrogen atom population densities during the actual combustion process of propane burning in oxygen. The technique used for propane is similar to that suggested by Fristrom and Westenberg to measure the free radical concentration profiles in C–C hydrocarbon/oxygen combustion.

INTRODUCTION

An understanding of the chemical reactions and rate processes which occur in flames requires a knowledge of the composition of the gases in the flame zone. Such an understanding is important from the standpoint of controlling hydrocarbon combustion for maximum power outputs and minimum ecological damage. Individual particles found in the flame zone are molecules, ions, and free radicals. A typical concentration distribution of these species in a combustion flame would consist of Z numbers of molecules, 10^{-2} Z numbers of free radicals, and 10^{-7} Z numbers of ions. Concentration measurements of these various species, both stable and unstable, in flames of various types have been made by a number of experimental techniques[1].

Some of the methods which have been employed for measuring free radical concentration in flames are calorimetry[2], mass spectroscopy[3], absorption spectroscopy[4], flame photometry[5], and tracer reactions[6]. The relative merits and disadvantages of these methods have been discussed by Fristrom and Westenberg[7]. One of the most promising methods of measuring free radical concentrations in flames involves the use of electron spin resonance (ESR) spectroscopy. Some qualitative ESR measurements have been made by producing a flame directly in the ESR instrument cavity[8]. This method, however, does not allow quantitative determination

---

*Present address: Department of Chemistry, University of Natal, Durban, South Africa.

of the concentration profiles of the free radicals. Westenberg and Fristrom^9 developed a method by which hydrogen and oxygen free radical (atom) concentration profiles in gas flames could be determined. The method involves the combination of ESR spectroscopy and a sample probing technique. The ability to make measurements for concentration levels of atom and radical species inside the flame itself offers excellent prospects of studying flame exciters and suppressants. Quantitative concentration measurements are based on the use of molecular oxygen as a reference^{10} and on the theoretical developments brought out by Westenberg and De Haas^{11}. The investigators determined the oxygen and hydrogen radical concentration profiles in the premixed C–C hydrocarbon/oxygen flames.

In the present investigation, the same method was employed to determine similar profiles for the propane/oxygen flame.

EXPERIMENTAL

The instrument used in this investigation is a Model 771 Hitachi electron spin resonance spectrometer for which the magnet was specially designed to achieve field strengths up to 7000 G. The instrument was modified by the Perkin–Elmer Corporation in a manner described by Westenberg and Fristrom^{12}. The experimental arrangement is shown in Fig. 1.

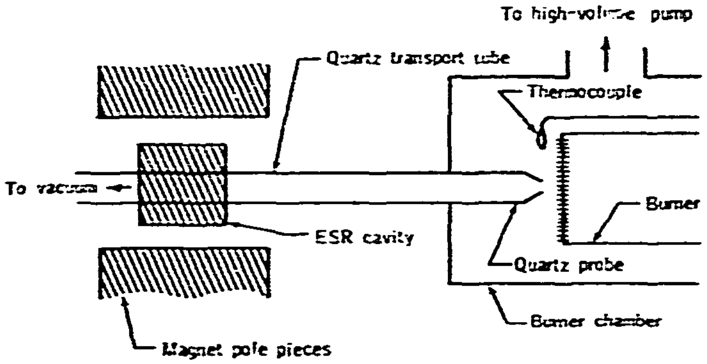

Fig. 1. Combination ESR and sample probe for experimentally determining chemical free radicals in flames.

In this investigation a flame is produced in a chamber under a pressure of 20 torr by a burner designed to produce a unidimensional flame. A quartz probe for which the distance from the burner can be adjusted is used to sample a portion or portions of the flame. The sampled gas is then passed down a quartz transport tube through the ESR cavity. The entire burner and transport tube assembly is moveable so that radical concentration measurements at different points along the transport tube can be made. This allows the extrapolation of the concentration values back to the probe tip as previously described^{13}. The oxygen and propane flow-rates are measured by a Matheson mass flowmeter (Models 8110 and 8112, respectively).

The present investigation involves study of flames for which there was an excess of oxygen (92.5 mole %). A PGM-10 Raytheon microwave power generator was used to dissociate oxygen which then was passed down the transport tube to clean it of free radicals and to serve as a scavenger. The molecular oxygen F line was used for calibration purposes and the calculations were carried out as previously described, using the relative Q values previously determined for oxygen and hydrogen radicals, namely 5.64×10^{-2} and 5.48×10^{-2}, respectively[14,15].

RESULTS AND DISCUSSION

Figure 2 illustrates the oxygen and hydrogen radical concentration profiles for the premixed propane/oxygen flame. No measureable oxygen or hydrogen radicals existed in the luminous zone of the flame. At the end of the luminous zone, where the fuel was exhausted, the oxygen and hydrogen radical concentrations increased rapidly to a maximum and then dropped off with distance, because of reaction and diffusion.

The profiles illustrated in Fig. 2 are similar to those previously obtained for ethane/oxygen, ethylene/oxygen, and acetylene/oxygen flames[16]. From these results

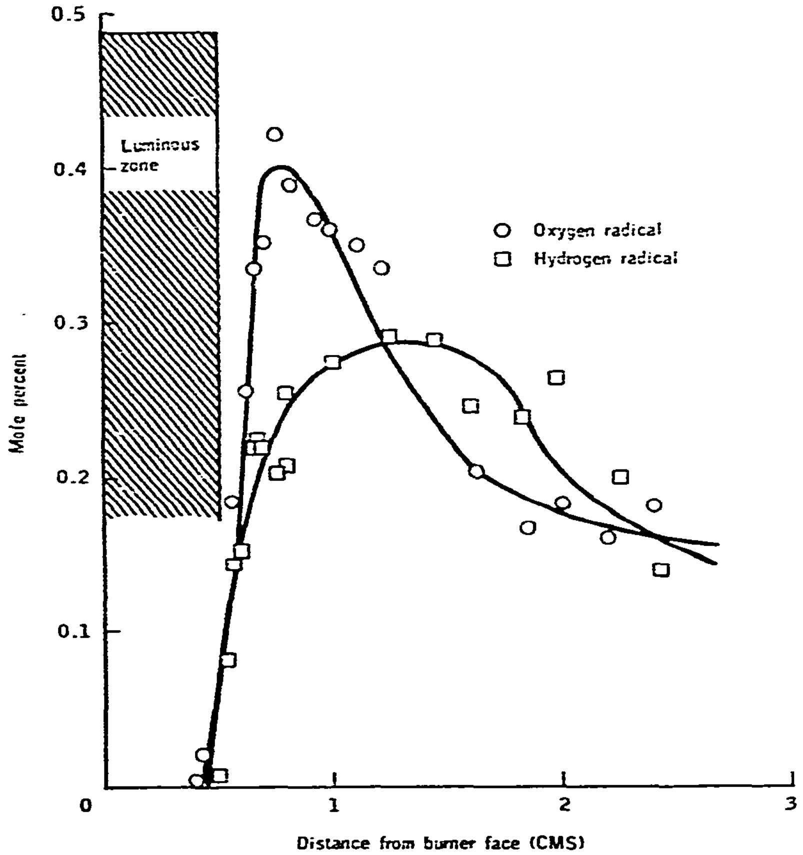

Fig. 2. Oxygen and hydrogen radical concentration profiles in the premixed propane/oxygen flame (92.5% oxygen).

several conclusions are drawn. On the basis of equilibrium considerations, because of the low concentrations in the luminous zone, neither the oxygen nor the hydrogen radical can be responsible for fuel removal. Instead, the hydroxyl radical probably enters into reaction with the hydrocarbon fuel. Since the hydrogen radical is light in weight and diffuses rapidly, it appears from the slopes of the hydrogen radical concentration profiles that some reaction in the post-luminous zone involves the hydrogen radical. This reaction is undoubtedly with the molecular oxygen[17]. In general the data obtained in this investigation support the conclusions of Westenberg and Fristrom.

Some generalized correlations may be made by comparing the maximum free radical concentrations for the fuels C_2H_2, C_2H_4, C_2H_6 and C_3H_8. The values are shown in Table I. Not surprisingly, the maximum hydrogen radical concentration increases with increasing numbers of hydrogen atoms in the hydrocarbon fuel molecule. The maximum oxygen radical concentration slightly decreases with increasing numbers of hydrogen atoms in the fuel molecule for the C_2 type hydrocarbons. This effect may be caused by more of the dissociated oxygen being present as hydroxyl free radical rather than as the oxygen radical, if more hydrogen is available. There is a striking increase in the maximum oxygen free radical concentration going from the C–C hydrocarbons to propane, an effect which must be due to the extra carbon atom in the propane molecule. This effect is understandable if molecular oxygen is dissociated in the reactions leading to CO_2 formation; hence, if more CO_2 is formed then more oxygen free radical is formed. Studies involving a greater number of gaseous hydrocarbons burning in oxygen are necessary before more positive conclusions can be reached. Studies of this type are presently in progress.

TABLE I

MAXIMUM OXYGEN AND HYDROGEN CONCENTRATION IN SOME GASEOUS HYDROCARBON/OXYGEN FLAMES

Fuel	*Maximum concentration (mole percent)*	
	Hydrogen radical	*Oxygen radical*
C_2H_2	0.08	0.35
C_2H_4	0.14	0.33
C_2H_6	0.24	0.28
C_3H_8	0.28	0.40

ACKNOWLEDGEMENT

The authors thank the National Research Council for having extended to E. L. Simmons a postdoctoral associateship to work in the Laboratories of the Structures and Mechanics Division at the Lyndon B. Johnson Space Center, NASA, Houston, Texas.

REFERENCES

1 R. M. Fristrom and A. A. Westenberg, *Flame Structure*, McGraw-Hill, New York, N.Y., 1965, p. 177 ff.
2 A. Snelton-Leah and N. Carpenter, *Fourth Symposium (International) on Combustion*, Williams and Wilkins, Baltimore, Md., 1953, p. 274.
3 G. C. Elenton, *J. Chem. Phys.*, 10 (1942) 403.
4 W. E. Kaskan, *Combust. Flame*, 2 (1958) 229.
5 E. M. Bulewicz, C. G. Jones and T. M. Sugden, *Proc. Roy. Soc.*, *A*, 227 (1954) 312.
6 A. A. Westenberg and R. M. Fristrom, *J. Phys. Chem.*, 65 (1961) 591.
7 R. M. Fristrom and A. A. Westenberg, see ref. 1, pp. 177–258.
8 V. V. Azatyn, V. N. Pamilov and A. B. Mal'bandyan, *Kinet. Katal.*, 2 (1961) 295.
9 A. A. Westenberg and R. M. Fristrom, *Tenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, Pa., 1965, pp. 473–487.
10 S. Krongelb and M. W. P. Strandberg, *J. Chem. Phys.*, 31 (1959) 1196.
11 A. A. Westenberg and N. de Haas, *J. Chem. Phys.*, 40 (1964) 3087.
12 A. A. Westenberg and R. M. Fristrom, see ref. 9, p. 474.
13 A. A. Westenberg and R. M. Fristrom, see ref. 9, pp. 474–475.
14 G. C. Elenton, see ref. 3, 10 (1942) 403.
15 A. A. Westenberg and N. de Haas, *J. Chem. Phys.*, 40 (1964) 3091
16 A. A. Westenberg and R. M. Fristrom, see ref. 9, pp. 476–477.
17 A. A. Westenberg and R. M. Fristrom, see ref. 9, p. 482.