The most prominent oxidation state of americium in anhydrous compounds is the III state, with only one example each of the IV and VI states. In solution, an additional state, the V, can be formed. This is in agreement with the general observation that the ease of oxidation of the transuranium elements to higher states is in part due to the stabilization by oxygenation to form ions of the type MO_2^+ and MO_2^{++} and to solvation by oxygenated solvents.

It seems unlikely that the anhydrous tetravalent chloride, bromide or iodide of americium can be prepared in view of the fact that no such compounds of plutonium have as yet been made. This would be in agreement with the observation that the III oxidation state becomes more prominent as the atomic number increases. It is possible, on the other hand, that the tetrafluoride may yet be prepared by the action of free fluorine or other vigorous fluorinating agents, in spite of the fact that several experiments in that direction have failed.

In most cases the X-ray diffraction pattern of the compounds was obtained from samples weighing only a few micrograms. Generally, it would be more satisfactory to use samples up to one hundred micrograms but it was found that a fairly penetrating electromagnetic radiation emitted by the samples tended to fog the X-ray film. The rather unusual situation of having too much material made it necessary to restrict the quantities to the order of ten micrograms, which seemed to be the optimum amount. The effect of fogging of the X-ray film is naturally much more noticeable in the case of compounds exhibiting low symmetry where the original intensity of the beam is distributed over many diffraction lines.

Acknowledgment.—The author wishes to take this opportunity to express his indebtedness to Prof. W. H. Zachariasen for his interest in this work and his analyses of the americium compounds, without which this investigation would have been impossible.

CHICAGO, ILLINOIS RECEIVED AUGUST 7, 1950

[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

Flame Propagation. II. The Determination of Fundamental Burning Velocities of Hydrocarbons by a Revised Tube Method

BY MELVIN GERSTEIN, OSCAR LEVINE AND EDGAR L. WONG

A method is described for the determination of fundamental rates of flame propagation in tubes. Data are presented for a variety of hydrocarbons including normal and branched alkanes, alkenes and alkynes as well as cyclohexane and benzene. The normal alkanes have a constant flame velocity except for methane which is slightly lower. Unsaturation increases the flame velocity in the order: alkanes < alkenes < alkynes. Branching reduces the flame velocity although the effect is small.

Introduction

The high velocity combustion required in modern aircraft power plants has led to revived interest in the study of rates of flame propagation. As part of our fundamental combustion program an investigation was undertaken to determine the rate of flame propagation in gaseous mixtures of a variety of hydrocarbons and air as a function of molecular structure. A study of the relationship between fundamental rate of flame propagation and unsaturation, chain length and chain branching of hydrocarbons is reported.

Coward and Hartwell[1] developed a method for obtaining fundamental flame velocities in a tube by photographing the flame and computing its surface area. Coward and Payman[2] related the fundamental flame velocity U_f to the linear observed flame velocity U_0 by the equation

$$U_f = (U_0 - U_g)A_t/A_f \qquad (1)$$

where U_g is the velocity of the unburned gas ahead of the flame, A_t is the cross-sectional area of the tube and A_f is the surface area of the flame. The fundamental velocity U_f is that velocity component normal to any tangent to the flame surface. It is a function of hydrocarbon type and concentration but is independent of the experimental apparatus. Because of the difficulty involved in its measurement, the gas velocity term was assumed to be negligible by earlier investigators using the tube method.

Attempts to reproduce the Coward and Hartwell method were only moderately successful. In the early phases of this research,[3,4] a Pyrex tube 12 feet long and 1 inch in diameter was used as the flame tube. Although it was possible to obtain relative trends in a hydrocarbon series using this technique, the results were dependent on the apparatus. The uniform flame movement over which the measurements were made occurred in only a small portion of the tube. The exact location of this uniform movement could not be predetermined for any particular hydrocarbon type. Moreover, the flame shape changed with hydrocarbon concentration so that the observed velocities were not proportional to the fundamental flame velocity. The uncertainty of the method is illustrated by the data of Wheatley[5] who reported the change in flame shape and was confirmed by preliminary experiments by the authors.

Guenoche, Manson and Mannot,[6] have demon-

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(1) Coward and Hartwell, *J. Chem. Soc.*, Pt. II, pp. 2676–2684 (1932).

(2) Coward and Payman, *Chem. Rev.*, **21**, 359 (1937).

(3) Reynolds and Gerstein, "Third Symposium on Combustion and Flame and Explosion Phenomena," The Williams and Wilkins Co., Baltimore, Md., 1949, p. 190.

(4) Reynolds and Ebersole, NACA Technical Note No. 1609 (1948).

(5) Wheatley, *Fuel*, **29**, 80 (1950).

(6) Guenoche, Manson and Mannot, *Compt. rend.*, **226**, 163 (1948).

strated theoretically and experimentally that an orifice placed at the ignition end of the tube would reduce the pressure waves which disturb the flame and render the motion non-uniform. Combining the information available in the literature on the propagation of flames in tubes, it was possible to develop a reproducible method for determining fundamental flame velocities.

Experimental

A schematic diagram of apparatus illustrating the flame tube, hydrocarbon and air system and location of the photocells is illustrated in Fig. 1.

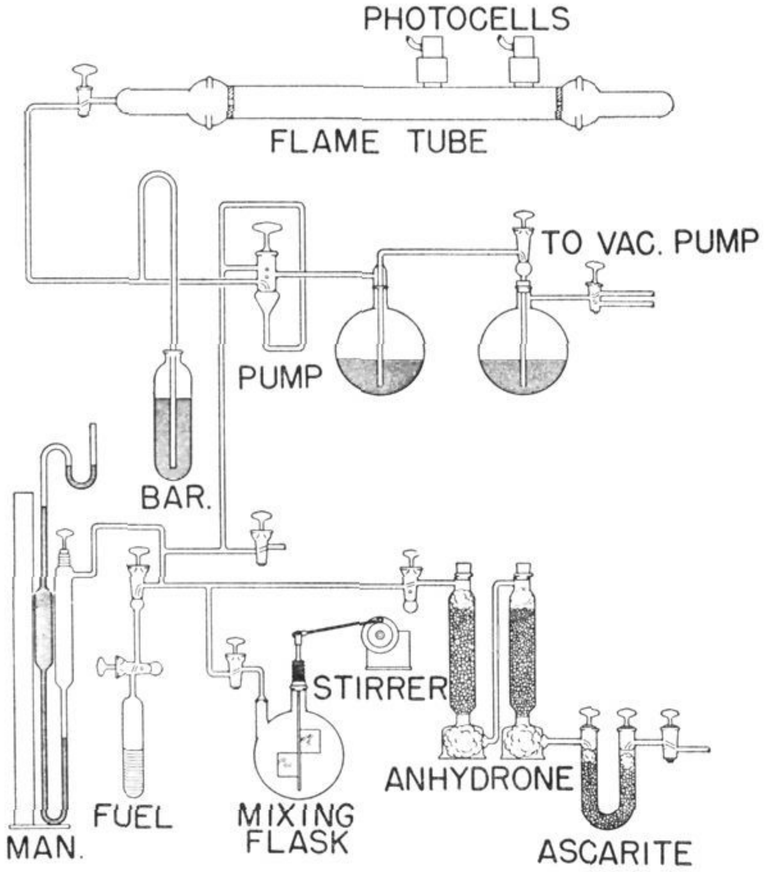


Fig. 1.—Sketch of flame speed apparatus.

Flame Tube.—The flame tube consisted of a 2.8 cm. o.d. Pyrex glass tube, 57 cm. long. A 35/25 semi-ball joint was attached to each end for connection to the vacuum apparatus. One end of the flame tube at which ignition was effected, contained an 8 mm. orifice. This was the orifice size calculated by Guenoche[6] to reduce pressure disturbances in the tube. After a series of tests an additional orifice, 1.7 mm. in diameter, was placed in the end of the tube toward which the flame advances. The use of the second orifice increased the uniformity of the flame travel.

Spatial Velocity.—The spatial velocity, U_0, was measured by means of photocells connected to an electronic timer. Since the time interval measured was about 0.1 second, the timer must accurately measure time intervals as small as 0.003 sec. to obtain a desired precision of ±1.5%. The photocells, placed 6 inches apart, acted as switches which controlled the flow of current from the 10,000 cycle oscillator into the pulse counter. The number of pulses recorded on the counter was directly proportional to the time interval between the excitation of the two photocells. The timer circuit was chosen because of its rapid response. To test the absolute accuracy of the timer, an oscillograph was placed in a parallel circuit with the timer and high speed motion pictures taken of the oscillograph screen as the flame progressed in the tube. The time markings on the film agreed with the recorded time interval within ±1.5%.

One of the primary difficulties with previous measurements of spatial velocities has been the uncertainty of the uniformity of the flame movement within the tube. To establish this uniformity the flame was photographed with a rotating drum camera. Since the film motion was held constant and directed at right angles to the direction of flame travel, a straight line trace on the film was an indication that the flame velocity had also been constant. Traces taken for representative hydrocarbons over the velocity range studied in this research indicated that the flame velocity remained constant in the region between the photocells.

Unburned Gas Velocity.—The gas velocity term, U_g, was determined by experimental measurement of the volumetric rate of gas flow within that portion of the flame tube toward which the flame was advancing. The volumetric rate of flow was determined from photographs of the progressive growth of a soap bubble blown from a tube connected to the flame tube. This volumetric rate of flow divided by the cross-sectional area of the flame tube, A_t, yielded a mean value for the gas velocity. To determine U_g, a glass tube bent at right angles so that the open end faced downward was inserted into the small orifice. The glass tube had a gradually increasing diameter from 1.5 mm. to 10 mm. The dimensions of this tube were determined experimentally to ensure that its use would not affect the area or velocity of the flame. Immediately prior to ignition, a soap film was placed across the large end of the glass tube. As the flame progressed in the tube, a soap bubble was formed by the ejection of gas from that portion of the tube toward which the flame was advancing. The soap bubble and an oscilloscope screen were photographed simultaneously at 64 frames per second. The volume of the soap bubble was calculated at the two points of excitation on the oscilloscope screen caused by the flame passing the two photocells. The increase in volume of the soap bubble and a time reading obtained simultaneously with the electronic timer yielded a value of the volumetric rate of gas flow. The variation of U_g with the spatial flame velocity is shown in Fig. 2. The data presented were taken for three different types of fuels covering a wide range of spatial velocities. A straight line, faired through the data over a range of spatial velocities from 70 to 150 cm./sec. can be represented by equation 2.

$$U_g = 0.236U_0 - 10.47 \qquad (2)$$

Although there is considerable scatter in the data, the original correction is a small one so that none of the deviations produce more than 2 to 3% error in the final result.

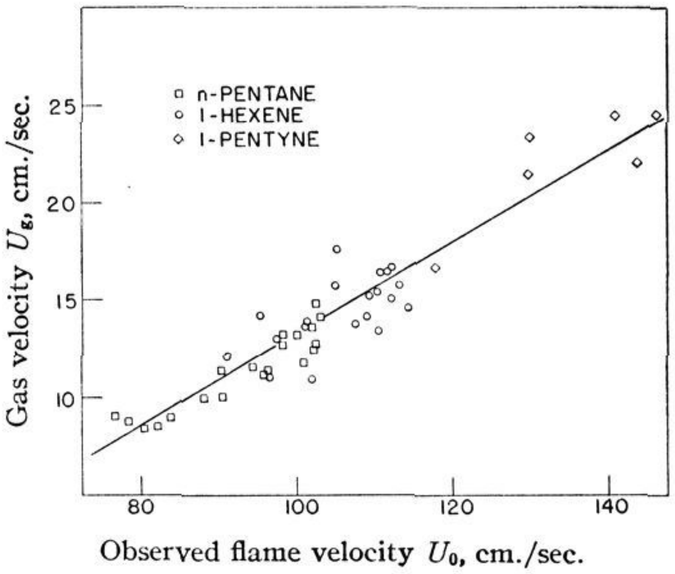


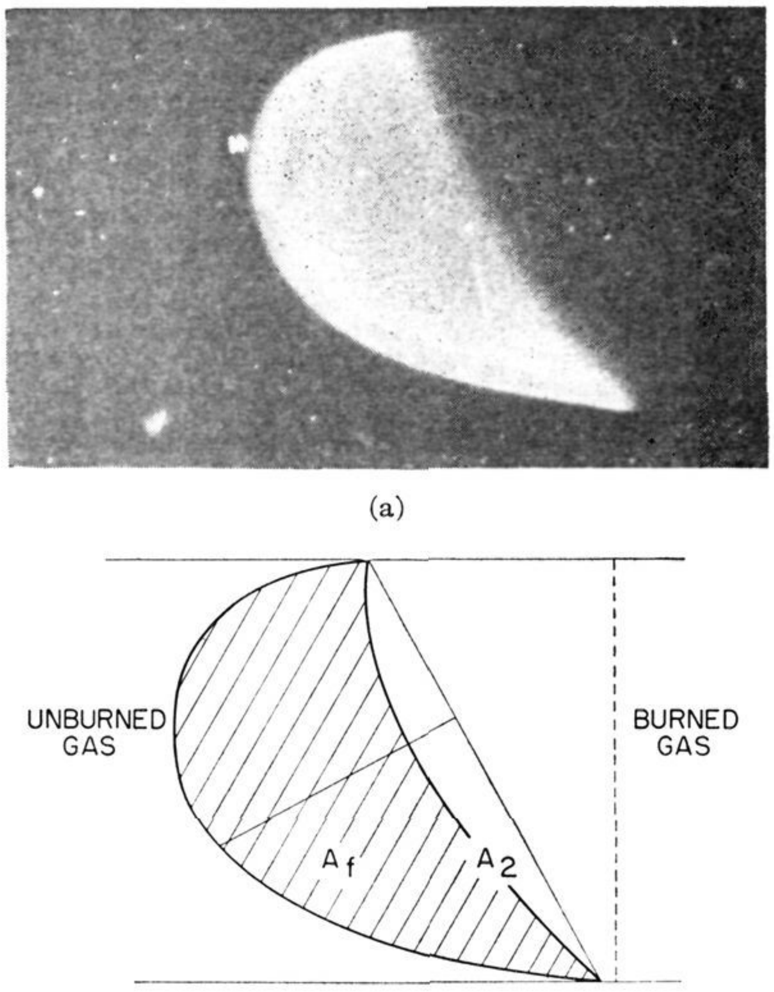
Fig. 2.—Variation of the unburned gas velocity with the observed linear flame velocity.

Area Measurements.—The cross-sectional area of the tube, A_t, was obtained by direct measurement of the internal diameter of the tube.

The flame surface area was obtained from photographs of the flame surface (Fig. 3). The area ($A_f + A_2$) of the surface bounded by the flame surface and a straight line joining the two points at which the flame touches the tube was calculated by the method of Coward and Hartwell.[2] To get the surface area of the flame itself (A_f), the element of area A_2 was calculated by assuming that this element was half of a prolate spheroid. The areas A_f and A_2 were constants for all of the hydrocarbons studied in this research.

Hydrocarbons.—The hydrocarbons used in this study were obtained from several sources and were all 97% or higher in purity.

Precision.—In order to check the reproducibility of the experimental procedure, *n*-hexane was tested periodically during the investigation. At no time did the values obtained for this hydrocarbon differ by more than 2%. At


(a)

(b)

Fig. 3.—Flame geometry: (a) photograph of flame; (b) sketch of flame showing critical areas.

least three determinations were made for each mixture studied. The flame velocities reported here are average values and have a precision of ±2%.

Procedure.—To prepare a mixture of hydrocarbon and air, the vaporized liquid or gaseous compound was admitted into the evacuated system. The hydrocarbon pressure was obtained from the absolute manometer. To reduce meniscus effects the manometer tubing involved in the measurement of pressures below 100 mm. had a diameter of 14 mm. Pressures in this range were read with the aid of a cathetometer with a precision of ±0.02 mm. Air, with carbon dioxide and water vapor removed by Ascarite and Anhydrone, respectively, was then admitted to the system. The total pressure was recorded. The hydrocarbon–air mixture contained in the 5-liter flask was then agitated by means of a motor-driven bellows stirrer. Infrared absorption spectra of samples withdrawn after 5 and 15 minutes of stirring indicated that a 5-minute period was sufficient to yield a completely homogeneous mixture. The hydrocarbon–air mixture was then transferred to the horizontal flame tube by means of a modified Toepler pump. The barometer indicated that the mixture within the flame tube was at atmospheric pressure. A sufficient period of time (usually 1 minute) was allowed for the mixture within the flame tube to become quiescent. Immediately prior to ignition, the flame tube was opened to the atmosphere at both ends and ignition was accomplished by means of a small alcohol lamp.

Results and Discussion

Typical curves for ethylene of flame velocity *versus* the volume per cent. of hydrocarbon in the inflammable mixture are shown in Fig. 4. Three curves are shown from this research illustrating the variation of U_0, $U_0 - U_g$ and U_f with hydrocarbon concentration. For comparison purposes the data of Linnett and Hoare[7] for ethylene are also shown. The numerical values and shape of the curve show good agreement. Linnett and Hoare's values

TABLE I

SUMMARY OF RESULTS

Fuel	Max. U_0, cm./sec.	Max. U_f,[a] cm./sec.	Vol. % fuel at max. U_f
Methane	84.5	33.8	9.96
Ethane	102.8	40.1	6.28
Propane	99.5	39.0	4.54
Butane	96.2	37.9	3.52
Pentane	98.0	38.5	2.92
Hexane	98.0	38.5	2.51
Heptane	98.3	38.6	2.26
2-Methylpropane	87.5	34.9	3.48
2,2-Dimethylpropane	83.0	33.3	2.85
2-Methylbutane	92.5	36.6	2.89
2,2-Dimethylbutane	90.0	35.7	2.43
2,3-Dimethylbutane	91.7	36.3	2.45
2,2,3-Trimethylbutane	90.5	35.9	2.15
2-Methylpentane	93.0	36.8	2.46
3-Methylpentane	92.7	36.7	2.48
2,3-Dimethylpentane	92.2	36.5	2.22
2,4-Dimethylpentane	89.9	35.7	2.17
Ethene	184.5	68.3	7.40
Propene	113.4	43.8	5.04
1-Butene	111.5	43.2	3.87
1-Pentene	110.0	42.6	3.07
1-Hexene	108.5	42.1	2.67
2-Methyl-1-propene	95.0	37.5	3.83
2-Methyl-1-butene	99.5	39.0	3.12
3-Methyl-1-butene	106.9	41.5	3.11
2-Ethyl-1-butene	100.3	39.3	2.65
2-Methyl-1-pentene	101.2	39.6	2.80
4-Methyl-1-pentene	104.0	40.5	2.62
Propyne	189.1	69.9	5.86
1-Butyne	155.0	58.1	4.36
1-Pentyne	140.0	52.9	3.51
1-Hexyne	127.0	48.5	2.97
4-Methyl-1-pentyne	116.9	45.0	2.87
2-Butyne	135.6	51.5	4.36
3-Hexyne	118.0	45.4	3.05
Cyclohexane	98.4	38.7	2.65
Benzene	104.5	40.7	3.34

[a] Calculated from equation 1 using the average values $A = 5.07$ sq. cm. and $A_f = 11.25$ sq. cm.

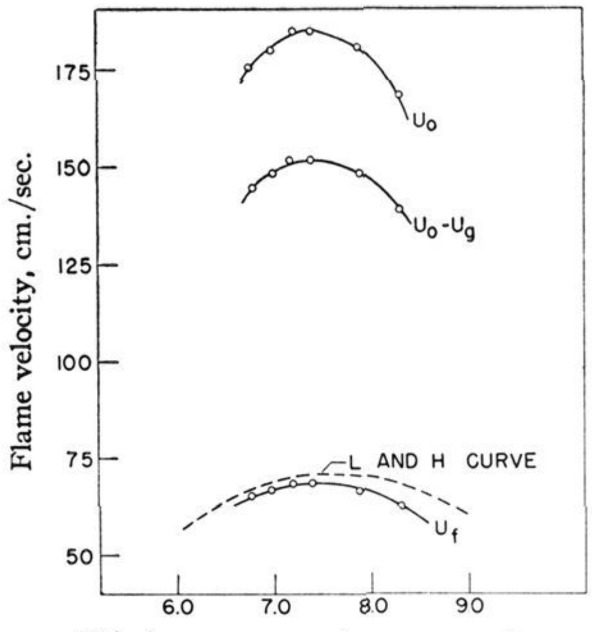


Fig. 4.—Flame velocity curves for ethylene including a comparison of the fundamental flame velocity with the data of Linnett and Hoare (ref. 7).

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(7) Linnett and Hoare, "Third Symposium on Combustion and Flame and Explosion Phenomena," ref. 3, pp. 195–204.

obtained by the bunsen burner technique are about 3 cm./sec. greater for mixtures containing less hydrocarbon than that required for maximum flame velocity. The larger deviation for mixtures containing excess hydrocarbon might be explained by dilution of the bunsen burner flame by external air which would result in higher flame velocities for such mixtures. Dilution by external air is, of course, not possible in the tube.

A comparison of the flame velocities obtained by the method described in this research with flame velocities reported in the literature is given in Table II. The agreement is satisfactory despite the fact that most of the literature values were obtained by the bunsen burner method. The use of the tube method is especially important in the study of pure fuels since a complete determination can be made on only a few milliliters of fuel. The most serious difficulty with the tube method lies in the measurement of the flame surface area since the choice of the proper geometric figure could alter the results. This is, of course, true to a lesser degree with the bunsen burner method also. The agreement between the two independent methods indicates that the assumptions made in both are justified.

TABLE II

COMPARISON OF FLAME VELOCITIES

Fuel	This research, U_t,[a] cm./sec.	Literature, U_t, cm./sec.
Methane	33.8	28[b]
		39[c]
		37[d]
Propane	39.0	36.6[e]
		44.0[c]
		45[f]
Hexane	38.5	32.0[d]
Ethylene	68.3	60[g]
		63[d]
		69[c]
		72[h]

[a] Calculated from equation (1) using $A_f + A_2 = 13.09$, $A_2 = 1.84$, $A_f = 11.25$ and $A_t = 5.07$. [b] Coward and Hartwell, *J. Chem. Soc.*, 2676 (1932). Only tube result reported in this column. [c] Smith, *Chem. Revs.*, 21, 400 (1937). [d] Jost and Croft, "Explosion and Combustion Processes in Gases," McGraw-Hill Book Co., New York, N. Y., 1946, p. 122. [e] Morrison and Dunlap, "Measurement of Flame Speeds with the V-Flame," Univ. of Mich. Report No. UMM-21, May, 1948. [f] Andersen and Fein, *J. Chem. Phys.*, 17, 1271 (1949). [g] Garside, Forsyth and Townend, *J. Inst. Fuel*, 18, 175 (1945). [h] Linnett and Hoare, "Third Combustion Symposium," Williams and Wilkins Co., Baltimore, Md., 1949, p. 195.

The flame velocities of the normal alkanes from methane through heptane plotted against the volume per cent. of hydrocarbon in the gaseous mixture are shown in Fig. 5. The shift of the maximum flame velocity to higher hydrocarbon concentrations as the molecular weight of the hydrocarbon decreases is primarily due to the difference in oxygen requirements of the various compounds. In general, the maximum flame velocity occurs in mixtures containing 10 to 30% more hydrocarbon than that required for the stoichiometric reaction. The flame velocities for the normal 1-alkenes and 1-alkynes are shown in Figs. 6 and 7, respectively.

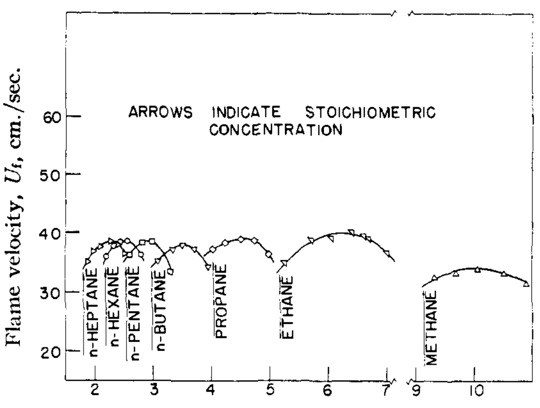


Fig. 5.—Fundamental flame velocities of the *n*-alkanes.

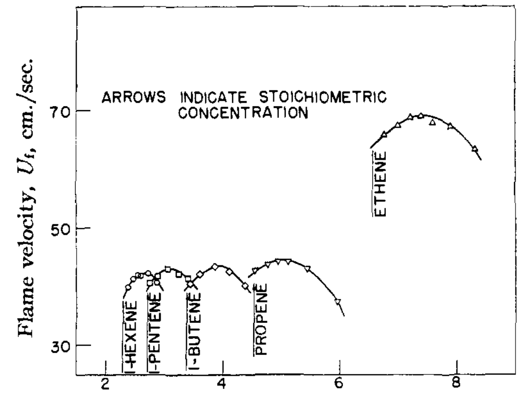


Fig. 6.—Fundamental flame velocities of the normal 1-alkenes.

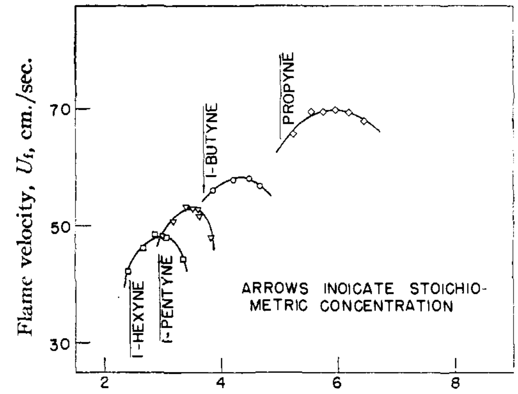
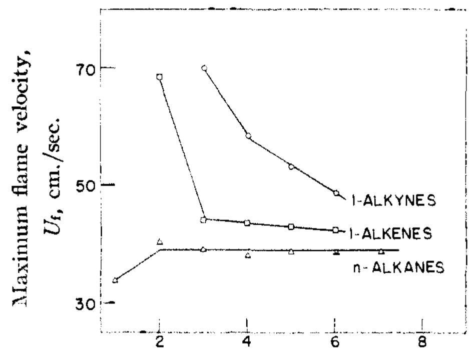


Fig. 7.—Fundamental flame velocities of the normal 1-alkynes.

A summary of the data for the normal aliphatic hydrocarbons illustrating the effect of unsaturation and molecular weight on flame velocity is shown in Fig. 8. The maximum flame velocity of each of the hydrocarbons in the previous figures is plotted against the number of carbon atoms in the molecule. The normal alkanes from ethane through heptane have approximately the same maximum flame velocity. Methane has a maximum flame velocity about 16% lower than the other members of this series. This result is of particular interest because



Number of carbon atoms in straight chain.

Fig. 8.—Summary of the maximum fundamental flame velocities of normal aliphatic hydrocarbons.

the data of Hartmann[8] show methane with a higher flame velocity than the other alkanes, while Smith[9] reports a trend similar to that found in this research. The effect of unsaturation on the maximum flame velocity is evident. For any given number of carbon atoms, the flame velocities are in the order: alkynes > alkenes > alkanes. The increase of maximum flame velocity with unsaturation is most pronounced in the compounds of low molecular weight, the effect decreasing as the length of the carbon chain increases. Even in hydrocarbons with six carbon atoms, however, the alkyne has a flame velocity about 25% greater than the corresponding alkane.

The effect of branching on the flame velocities of the alkanes is illustrated by the data presented in Table I. Although curves were obtained as a function of hydrocarbon concentration, only the maximum flame velocities are reported. Only the decrease from propane to 2-methylpropane is outside the experimental error. The other trends, however, are in the direction one might predict on the basis of the above decrease. The substitution of methyl groups for hydrogen appears to lower the flame velocity, the effect being greater in the propane series than in parent molecules of higher molecular weight. Of particular interest is the flame velocity of neopentane which has a peak flame velocity almost identical with that of methane. This result may be an indication of the importance of symmetry in flame propagation.

The variation of maximum flame velocity with branching in the 1-alkene series is also presented in Table I. Only the changes in flame velocity from propene to 2-methyl-1-propene and from 1-butene to 2-methyl-1-butene are outside the experimental error. Here again, however, the other trends are in a direction one would expect on the basis of the above results. For a chain containing a given number of carbon atoms, the substitution of a methyl or ethyl group for hydrogen reduces the flame velocity. The reduction in flame velocity appears greatest when the substitution occurs on a carbon atom adjacent to the double bond. The effect of substitution on maximum flame speed decreases as the length of the original carbon chain increases. The effect of an ethyl group substituted in butene-1 appears to be the same as that of a methyl group substituted in the same position. Although the effects of branching in the alkane and alkene series are in a reasonable direction, more precise flame velocity measurements are required to verify these trends.

A summary of the data for all of the compounds studied in this series, including the observed spatial velocities, U_0, the unburned gas velocity, U_g, and the fundamental flame velocity, U_f, are given in Table I.

Acknowledgment.—The authors wish to express their appreciation to Messrs. E. Hoss and E. Carlson for the design, construction and maintenance of the electronic timer.

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[8] Jost and Croft, "Explosion and Combustion Processes in Gases," McGraw-Hill Co., New York, N. Y., 1946, p. 122.

[9] Smith, *Chem. Revs.*, **21**, 400 (1937).

CLEVELAND, OHIO RECEIVED JULY 17, 1950

[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

Flame Propagation. III. Theoretical Consideration of the Burning Velocities of Hydrocarbons[1]

BY DOROTHY MARTIN SIMON

The maximum flame velocities for 35 hydrocarbons including *n*-alkanes, branched alkanes, *n*-alkenes branched alkenes, alkenes, benzene and cyclohexane are shown to be consistent with the active particle diffusion theory of flame propagation. The rate constants calculated from the Tanford and Pease equation for all the hydrocarbons are the same $1.4 \pm 0.1 \times 10^{11}$ cc. mole^{-1} sec.$^{-1}$ except for ethylene. The behavior of ethylene is different from the other hydrocarbons.

The second paper of this series[2] reported the determination of maximum fundamental flame velocities for a number of hydrocarbons in air by a tube method. The experimental relation between fundamental flame velocity and such molecular structure factors as chain length, unsaturation and chain branching was shown. The purpose of this paper is to relate those observations with a theory of flame propagation.

There are two general theories of flame propagation—a thermal theory and an active particle diffusion theory. The thermal theory historically attributed to Mallard and Le Chatelier[3] is based on the assumption that molecular heat conduction is the rate determining process for flame propagation. The gas ahead of the flame front is considered to be heated to a temperature of spontaneous inflammation (designated as the ignition temperature) by conduction of heat from the flame.

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[1] Presented in part at the 117th Meeting of the American Chemical Society in Detroit, Mich., 1950.

[2] Gerstein, Levine and Wong, THIS JOURNAL, **73**, 418 (1951).

[3] Mallard and Le Chatelier, *Ann. Mines*, [8] **4**, 274 (1883).