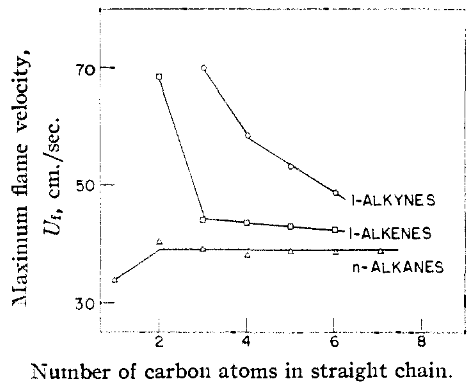

Fig. 8.—Summary of the maximum fundamental flame velocities of normal aliphatic hydrocarbons.

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).

[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 ± 0.1 × 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).

This theory has not been widely accepted in recent years because it depends on the questionable concept of a unique ignition temperature. The evaluation of any specific equation of the thermal type for a series of compounds is difficult, for a knowledge of heat capacities, thermal conductivities, flame temperatures and ignition temperatures is necessary.

In the active particle diffusion theory, first suggested by Lewis and Von Elbe,[4] the rate of flame propagation is considered to depend on the rate of diffusion of active particles. These active particles are the chain carriers of the oxidation reaction. Since hydrogen atoms, oxygen atoms and hydroxyl radicals are formed in the flame, and the rate of flame propagation appears to depend on the calculated equilibrium flame concentrations of these three particles, they have been considered to be the active particles. If an active particle diffusion theory is operative, the rate of flame propagation should depend on (1) the concentration of active particles, (2) the rate of diffusion of these particles and (3) the rate of reaction of the combustible and the active particles.

There are several papers in the literature which correlate active particle concentration and flame velocities for one combustible with oxygen and nitrogen in various concentrations. Linnett and Hoare[5] have published such a correlation for ethylene–oxygen–nitrogen mixtures. They found that the relative concentration of active particles plotted against fundamental flame speed gave the dotted curve in Fig. 1. The relative active particle concentrations were considered to be the sum of the equilibrium concentrations of hydrogen atoms and hydroxyl radicals times their relative diffusion coefficients. Linnett and Hoare calculated the ratio of the diffusion coefficients to be 6.5:1:1 for hydrogen, oxygen and hydroxyl.

In this investigation the equilibrium product concentrations were calculated for all hydrocarbons at the concentrations which were reported[2] to give the maximum flame speed. The calculations were made by the matrix method with the tables of thermodynamic constants published by Huff[6] and heats of formation published by the Bureau of Standards.[7] The largest uncertainty in the calculation of the relative atom concentrations is the original choice of the concentration of hydrocarbon in air for maximum flame velocity. An uncertainty in concentration of hydrocarbon of at least 2% is probable. The heptane data indicate the magnitude of this effect. For a 1.8% decrease in heptane concentration from 2.26%, a 3.8% increase in relative atom concentration was calculated.

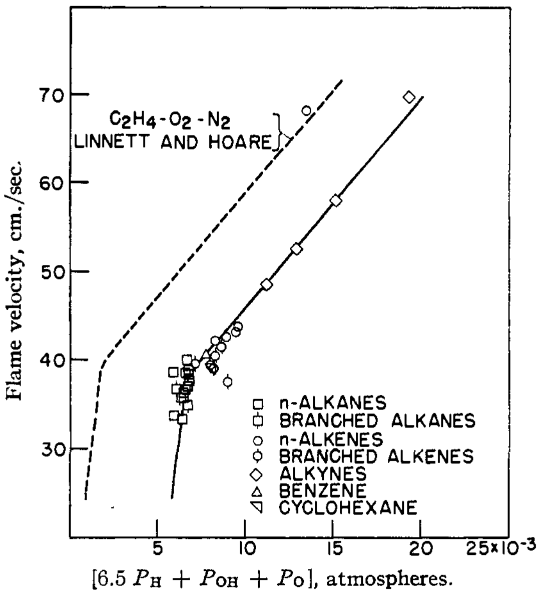

Fig. 1.—Variation of flame velocity with relative atom and radical concentrations.

Relative active particle concentrations were calculated and plotted against the fundamental flame velocity. A curve parallel to the ethylene curve was drawn through the hydrocarbon data (Fig. 1) in order to demonstrate the similarity of the two correlations. Although the rate of reaction of active particles with hydrocarbons has not been considered, all the hydrocarbon points appear to lie on one curve except for the ethylene point which lies on the original Linnett and Hoare curve. The position of the ethylene point suggests that there may be a fundamental difference in the behavior of ethylene and the other hydrocarbons studied.

The flame speed and hydrogen atom concentration data of Sachsse and Bartholomé[8] for methane–oxygen–nitrogen, propane–oxygen–nitrogen, octane–oxygen–nitrogen and acetylene–oxygen–nitrogen (oxygen content higher than for air mixtures) giving flame speeds of 45 to 333 cm./sec. also indicated that the flame velocity for these mixtures may be roughly correlated with hydrogen atom concentration without considering the rate of reaction. Acetylene–oxygen mixtures appeared to deviate, however, in a manner similar to ethylene. The fact that most hydrocarbon systems appear to give one correlation suggests that the rate of reaction of the active particles with the hydrocarbons is either the same or unimportant in the mechanism of flame propagation except for a few cases.

Tanford and Pease[9] have derived an equation relating the fundamental flame velocity and the concentration of active particles which has been called the square root law of flame propagation.

$$U_f = \sqrt{\sum_i \frac{k_i D_i p_i}{B_i} \frac{LQ'}{Q}} \qquad (1)$$

where

U_f = fundamental flame velocity
k_i = rate of reaction of combustible and the ith active particle
D_i = rate of diffusion of ith active particle
p_i = equilibrium partial pressure of ith active particle
L = number of molecules of gas at flame temperature
Q' = mole fraction of combustible
Q = mole fraction of potential combustion product
B_i = a term arising from recombination of ith free radical

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[4] Lewis and Von Elbe, *J. Chem. Phys.*, **2**, 283 (1934).

[5] Linnett and Hoare, "Third Symposium on Combustion, Flame and Explosion Phenomena," Williams and Wilkins, Baltimore, Maryland, 1949, p. 195.

[6] Huff, National Advisory Committee for Aeronautics TN 2113, 1950.

[7] Selected Values of Properties of Hydrocarbons, Circular of the National Bureau of Standards, C461 (1947).

[8] Sachsse and Bartholomé, *Z. Elektrochem.*, **53**, 183 (1949).

[9] Tanford and Pease, *J. Chem. Phys.*, **15**, 861 (1947).

TABLE I

BURNING VELOCITIES OF HYDROCARBON FLAMES

Compounds	Vol. % hydrocarbon	T_e[a], °K.	$p_H \times 10^3$ atm.	$p_O \times 10^4$ atm.	$p_{OH} \times 10^3$ atm.	$k \times 10^{13}$, cc. molecules^{-1} sec.$^{-1}$	Flame velocity, cm./sec. Exptl.	Calcd.
Methane	9.96	2235	0.57	1.42	1.98	2.36	33.8	33.9
Ethane	6.28	2246	.79	0.83	1.43	2.78	40.1	37.1
Propane	4.54	2251	.82	.80	1.37	2.56	39.0	37.7
Butane	3.52	2256	.82	.89	1.43	2.42	37.9	37.6
Pentane	2.92	2249	.82	.72	1.26	2.51	38.5	37.5
Hexane	2.51	2241	.83	.59	1.12	2.53	38.5	37.3
Heptane	2.26	2208	.80	.29	0.75	2.44	38.6	38.0
2-Methylpropane	3.48	2259	.79	1.02	1.53	2.13	34.9	36.9
2,2-Dimethylpropane	2.85	2254	.76	0.96	1.46	2.02	33.3	36.2
2-Methylbutane	2.89	2253	.80	.84	1.37	2.31	36.6	37.1
2,2-Dimethylbutane	2.43	2254	.78	.90	1.40	2.24	35.7	36.8
2,3-Dimethylbutane	2.45	2252	.80	.81	1.33	2.30	36.3	37.0
2,2,3-Trimethylbutane	2.15	2242	.80	.64	1.17	2.29	35.9	36.6
2-Methylpentane	2.46	2251	.81	.78	1.30	2.33	36.8	37.2
3-Methylpentane	2.48	2245	.82	.67	1.20	2.34	36.7	37.1
2,3-Dimethylpentane	2.22	2220	.80	.38	0.88	2.42	36.5	36.2
2,4-Dimethylpentane	2.17	2236	.80	.55	1.07	2.29	35.7	36.4
Ethylene	7.40	2387	1.56	3.51	2.95	3.97	68.3	52.9
Propene	5.04	2341	1.21	2.26	2.29	2.22	43.8	45.3
1-Butene	3.87	2320	1.14	1.64	1.92	2.43	43.2	42.8
1-Pentene	3.07	2316	1.04	1.82	2.01	2.36	42.6	42.8
1-Hexene	2.67	2287	1.04	0.96	1.43	2.43	42.1	41.7
2-Methylpropene	3.83	2315	1.06	1.71	1.95	1.90	37.5	42.0
2-Methyl-1-butene	3.12	2298	1.02	1.28	1.66	2.13	39.0	41.2
3-Methyl-1-butene	3.11	2305	1.04	1.44	1.78	2.31	41.5	42.2
2-Ethyl-1-butene	2.65	2284	1.00	0.98	1.44	2.22	39.3	40.7
2-Methyl-1-pentene	2.80	2237	.96	0.36	0.84	2.43	39.6	39.2
4-Methyl-1-pentene	2.62	2295	1.00	1.23	1.63	2.23	40.5	41.3
Propyne	5.86	2472	2.28	6.65	3.78	3.10	69.9	61.3
1-Butyne	4.36	2413	1.84	3.53	2.76	2.60	58.1	55.6
1-Pentyne	3.51	2370	1.61	2.03	2.07	2.50	52.9	51.6
1-Hexyne	2.97	2333	1.46	1.17	1.55	2.37	48.5	48.6
2-Butyne[b]	4.36	2401	1.73	3.11	2.57	2.23	51.5	53.3
Cyclohexane	2.65	2249	0.83	0.65	1.13	2.56	38.7	37.4
Benzene	3.34	2307	1.02	0.96	1.15	2.42	40.7	40.4

[a] Calculated equilibrium flame temperature. [b] 3-Hexyne and 4-methyl-1-pentyne have been omitted since accurate heat of formation data were not available.

They have applied the equation to moist carbon monoxide–oxygen–nitrogen, hydrogen–oxygen–nitrogen and methane–oxygen–nitrogen flame velocity data for a range of concentrations for each system and have calculated k values of 3.9, 1.0 and 1.9 × 10^{11} cc. mole^{-1} sec.$^{-1}$ for hydrogen, carbon monoxide and methane.[10]

To apply this equation to a series of hydrocarbons it is necessary to include a term for the total number of moles of water and carbon dioxide which form per mole of the specific hydrocarbon. Assuming H, O and OH are the chain carriers and that they are equally effective ($k_O = k_H = k_{OH}$), the Tanford and Pease relation becomes

$$U_t = \left[\frac{nQ'L}{Q} k \left(\frac{D_H p_H}{B_H} + \frac{D_O p_O}{B_O} + \frac{D_{OH} p_{OH}}{B_{OH}}\right)\right]^{1/2} \quad (2)$$

where

n = number of moles of combustion product per mole of combustible.

The modified Tanford and Pease equation has been evaluated using the flame velocity and concentration data for all the hydrocarbons.

The diffusion coefficients for H, OH and O into pure O_2 and N_2 were calculated by the Stefan–Maxwell equation.[11] Diffusion molecular diameters[12] and the Bohr radius 53 Å. for hydrogen were used. The final values for diffusion into air were determined by interpolation to be 1.78, 0.28 and 0.40 sq. cm. per sec. for H, OH and O. B values were calculated by the method outlined by Tanford.[13]

The measured fundamental flame velocities were used to calculate k values for all hydrocarbons (Table I). The constancy of the calculated rate constants was expected since the correlation of flame velocities with relative atom concentrations indicated that the rate constants were either the same or unimportant in the mechanism of flame propagation. If the rate constants are important as Tanford and Pease have indicated, then the over-all specific rate constants for the oxidation of all the hydrocarbons studied must be approxi-

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(10) Tanford, ref. 5, p. 140.

(11) Jeans, "Kinetic Theory of Gases," Cambridge University Press, Cambridge, 1947, p. 207.

(12) Chapman and Cowling, "The Mathematical Theory of Non-Uniform Gases," Cambridge University Press, Cambridge, 1939, p. 252.

(13) Tanford, *J. Chem. Phys.*, **15**, 433 (1947).

mately the same except for ethylene. The *k* for best fit of the data was calculated to be $2.38 \pm 0.16 \times 10^{-13}$ cc. molecule^{-1} sec^{-1} or $1.4 \pm 0.1 \times 10^{11}$ cc. mole^{-1} sec.$^{-1}$.[14]

Table I also gives a comparison of the measured flame velocities and the values calculated by the modified Tanford and Pease equation using the average *k* value. The agreement between the calculated and the observed flame velocities is striking. Twenty-eight of the 35 calculated flame speeds are within ±5% of the measured flame velocities, six more are within 12% and only ethylene deviates by a higher per cent., 23%. This agreement is surprising since no differentiation between the rates of reaction of the three chain carriers has been made, the rates of reaction between active particle and hydrocarbons have been considered constant, and the choice of the concentration of hydrocarbon in air which has the maximum flame velocity introduced an uncertainty. The deviation of the calculated flame velocity from the observed value for ethylene is about six times the average deviation for the other hydrocarbons which indicates that ethylene behaves in a different manner than the other hydrocarbons. The over-all reaction constant for the oxidation of ethylene appears to be much higher than for the other hydrocarbons. It may be significant that four of the six calculated flame velocities which had large deviations (5–12%) from the measured values were for short chain branched hydrocarbons. Perhaps the rate constants for these oxidations are actually a few per cent. lower. The active particle diffusion theory of flame propagation appears to explain the observed relation of fundamental flame velocity with molecular structure for the aliphatic hydrocarbons, benzene and cyclohexane. The observed trends in flame velocity with increasing chain length, degree of unsaturation and methyl substitution are also predicted by this theory.

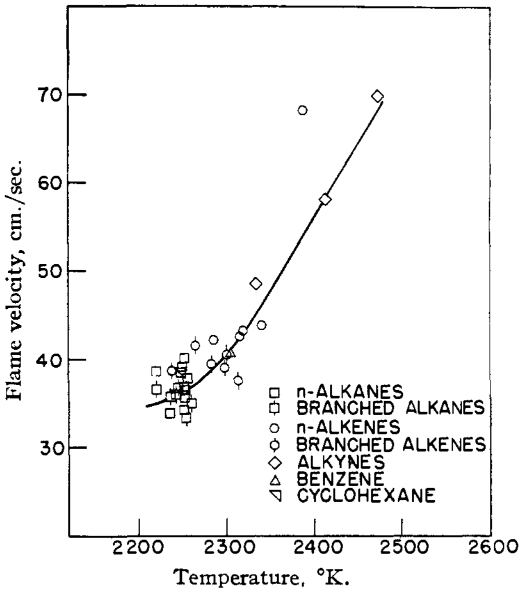

Fig. 2.—Variation of flame velocity with equilibrium flame temperature.

It must not be forgotten, however, that the calculated radical concentrations depend on the flame temperatures and that any thermal mechanism also depends on flame temperature. A correlation between the equilibrium flame temperature and the observed flame velocities for the hydrocarbons may be predicted. Figure 2 shows the correlation. Specific thermal mechanisms have not been applied to the series of hydrocarbons since the thermal properties of the mixtures at flame temperature are so uncertain, but it is obvious that some mechanism which depends strongly on flame temperature might give a correlation with flame speed which is equally as good as the active particle diffusion theory. Since such a correlation is possible, a thermal mechanism may not be ruled out.

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(14) The usual units are obtained by multiplying by Avogadro's number.