TABLE II

Λ_0 AND K' FOR VARIOUS SALTS IN ETHYLENEDIAMINE AT 25°

Salt	Λ_0	Λ_0[8] Other investigators	$K' \times 10^{-4}$
$AgNO_3$	63.5	(61.4)	5.740
AgI	72.8	(48.8)	0.168
$NaNO_3$	75.1		1.120
NaI	61.4		6.860
Bu_4NNO_3	59.3		5.110
Bu_4NI	57.8		5.320

in the case of the same electrolytes in ethylenediamine a range of 10 to 30 of these same units would be found over the same concentration range.

The plots of the reciprocal of the equivalent conductance against M gives a straight line with the intercepts at $1/\Lambda_0$. The values of Λ_0 obtained from these curves are slightly lower than those obtained from the Fuoss calculation. The cause of this deviation is, no doubt, the fact that no correction has been made for incomplete dissociation.

The plots of $-\log f^2$ *versus* $\sqrt{M\gamma}$ yield a straight line, an example of which is shown in Fig. 1 for tetra-*n*-butylammonium nitrate.

When $F(Z)/\Lambda$ is plotted against $M\Lambda f^2/F(Z)$ a straight line results (Fig. 1) whose slopes and intercepts were calculated by the method of least squares yielding Λ_0 and the dissociation constant, K', as shown in Table II.

The possibility of finding a solute possessing strong electrolytic properties in ethylenediamine is quite unlikely.

BLOOMINGTON, INDIANA

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

Flame Propagation. V. Structural Influences on Burning Velocity. Comparison of Measured and Calculated Burning Velocity

BY PAUL WAGNER AND GORDON L. DUGGER

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The fundamental burning velocities of thirty-one hydrocarbons of which two contained deuterium, six oxygenated compounds, isopropylamine and acrylonitrile have been determined. The burning velocities of twelve of the normally liquid hydrocarbons were measured in a burner type apparatus at elevated initial temperatures, and the fundamental burning velocities at 298°K. were determined by extrapolation of these data. With the exception of acrylonitrile, all other burning velocity measurements were made in a horizontal, open end tube. Some qualitative conclusions are drawn as to the effect of the molecular structures of the fuels on the burning velocities. Burning velocity trends previously established for 56 other pure hydrocarbons are in the main borne out, and are extended to include the general behavior of the cyclic hydrocarbons. The behavior of the oxygen and the nitrogen compounds is discussed. Equilibrium flame temperatures and active particle concentrations for the mixtures at which the maximum burning velocities occurred were calculated for thirty-seven of the compounds. The Tanford–Pease "square root law" of burning velocity, which relates active particle concentration with burning velocity, was used in a modified form to calculate the burning velocities for all but the deuterated compounds. An empirical average "rate constant" determined from the hydrocarbon data with the modified square root law equation had a value of 2.57×10^{-13} ml. molecule^{-1} sec.$^{-1}$ The burning velocities of the pure hydrocarbon compounds correlate better with relative active particle concentrations than do those compounds containing oxygen or nitrogen. This is reflected in the values of the calculated burning velocities for the latter compounds.

Introduction

One of the major problems of high speed flight propulsion research involves the behavior of the fuel–air mixture during the combustion process. In order to gain some basic understanding of this phenomenon, a program of study of fundamental combustion properties was undertaken at this laboratory. One of the properties investigated has been the rate of flame propagation of various gaseous hydrocarbons in air, and the relation of these rates to the molecular structures of the fuels. Previously published results include laminar burning velocities determined by both the tube[1,2] and the Bunsen burner method[3,4] and consideration of these data in terms of existing theories of flame propagation.[3-7] A simplified theoretical equation based on an active particle diffusion mechanism has been used to calculate burning velocities for a large number of pure hydrocarbons in air.[5,6] In the present work burning velocities in air of twenty nine pure hydrocarbons, two deuterated hydrocarbons, six oxygenated hydrocarbons, acrylonitrile and isopropylamine are presented and the semi-theoretical calculations are extended to include the majority of these latter data. Burning velocity measurements were made in either a horizontal tube, or in a Bunsen burner type apparatus.

Ideally, a comprehensive theory of flame propagation[8] should be used to calculate burning velocities. However, the information needed for the solutions of the differential equations in such a treatment is available for only the very simplest of systems. A less exact but more convenient approach is to use equations derived from either a thermal or an active particle diffusion model of the combustion mechanism. The thermal theory is based on the assumption that the rate at which heat

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(1) M. Gerstein, O. Levine and E. L. Wong, THIS JOURNAL, **73**, 418 (1951).

(2) M. Gerstein, O. Levine and E. L. Wong, *Ind. Eng. Chem.*, **43**, 2270 (1951).

(3) G. L. Dugger, THIS JOURNAL, **72**, 5271 (1950).

(4) G. L. Dugger and D. D. Graab, "Fourth Symposium on Combustion," Williams and Wilkins, Baltimore, Maryland, 1953, p. 302.

(5) D. M. Simon, THIS JOURNAL, **73**, 422 (1951).

(6) D. M. Simon, *Ind. Eng. Chem.*, **43**, 2718 (1951).

(7) G. L. Dugger and D. M. Simon, "Fourth Symposium on Combustion," Williams and Wilkins, Baltimore, Maryland, 1953, p. 336.

(8) Such a theory would include processes of diffusion, heat transfer and chemical kinetics in addition to the more general hydrodynamic considerations. A detailed treatment of the characteristics of steady state one-dimensional flames is given by J. O. Hirschfelder and C. F. Curtiss, *J. Chem. Phys.*, **17**, 1076 (1949).

is conducted from the reaction zone to the unreacted mixture determines the rate at which the flame will propagate. The active particle diffusion theory is based on the assumption that the rate determining factor is the rate at which active particles diffuse from the reaction zone into the unburned gas. Despite the apparent difference in basic assumptions, modified equations from both theories have been used to predict burning velocities with comparable accuracy.[7,9] The variables in both types of equations are similarly dependent on flame temperature so that this end result might be expected. The present work treats the experimental results in terms of the active particle diffusion mechanism.

Experimental

Burning velocity measurements were made by one of two methods. The tube method[1] was used for volatile compounds which were available only in limited quantity. The Bunsen burner method[4] was used for measurements on high boiling liquid fuels which were available in larger quantity and which had to be heated in order to obtain proper fuel concentration in the vapor phase.

Burning Velocity Measurements by the Tube Method.—The apparatus and its use have been dealt with in detail by Gerstein, Levine and Wong.[1] The inflammable mixture is contained in a horizontal tube which contains an orifice at each end. The function of the orifices is to prevent oscillations in the combustion wave. Upon ignition at one end the combustion wave travels at a uniform rate through most of the tube. The time taken to traverse a given distance through the tube is measured by means of two photocells which are connected to a counter through a gate circuit. The rate at which the unburned gas ahead of the combustion wave is propelled through the orifice and out of the tube has been determined experimentally,[1] and may be expressed in the form

$$u_g = Au_0 + B \qquad (1)$$

where u_g is the rate at which the unburned gas is expelled, u_0 is the spatial velocity of the combustion wave, and A and B are empirically determined constants. The area of the flame is determined from the luminous zone of the flame by photographic methods. The fundamental burning velocity is calculated from

$$u_f = (u_0 - u_g)\frac{A_t}{A_f} \qquad (2)$$

where u_f is the fundamental laminar burning velocity, and A_f and A_t are the areas of the flame surface and of the tube cross section, respectively. All the tube measurements were made at room temperature and at a total pressure of one atmosphere.

Burning Velocity by the Bunsen Burner Method.—This apparatus and its use have been fully described by Dugger and Graab.[4] Flame surface areas A_f were measured from the outside edge of the schlieren image obtained with a horizontal knife-edge, advanced from above. The schlieren system was of the two mirror *z*-type. Burning velocities were calculated by a total area method analogous to equation 2

$$u_f = V_0/A_f \qquad (3)$$

where V_0 is the volumetric flow rate of the unburned combustible–air mixture at the initial temperature T_0.

In order to measure the fundamental burning velocities of the higher molecular weight liquid fuels, it is necessary to warm the mixture to a temperature where the vapor pressure of the fuel is equal to or greater than that pressure necessary for the desired concentration. The fuel is mixed with preheated air, and the mixture kept at the appropriate temperature in the thermostated flow system until the combustion has taken place. Studies have been made on the effect of initial temperature on the fundamental burning velocities of propane–air[8] and 2,2,4-trimethylpentane–air[4] mixtures, and it has been found that over a short temperature range the fundamental burning velocity may be expressed as

$$u_f = cT_0^a \qquad (4)$$

where T_0 is the initial temperature of the mixture, and a and c are experimentally determined constants. Extrapolated values of burning velocities for initial temperatures equal to room temperature compared favorably with measured values. In the present work, the Bunsen burning velocities were measured at two initial temperatures where possible.

Burning velocities measured by the burner method as described here appear to yield values which are 10% higher than those measured in the tube apparatus. This figure is arrived at by comparison of values of burning velocity for the compounds ethylene, propane and benzene as determined by the two techniques. Since there is not sufficient information available to formulate a more general relationship, reported burning velocities will be discussed without further consideration of the measurement method. Although the reported trends would probably not be affected, the possibility that such a discrepancy may indicate an uncertainty in the reported values should not be dismissed.

Results and Discussion

The experimental results are summarized in Tables I and II. Listed in Table I are the measured Bunsen burner burning velocities and the initial mixture temperatures at which these measurements were made. The calculated values of the temperature exponents and coefficients are listed under "*a*" and "*c*," respectively. The last column is the value of the laminar fundamental burning velocity as calculated from equation 4 wherein the initial temperature is taken to be 298°K. Table II contains the concentration at which the maximum burning velocity was measured, and the value of the burning velocity. This table includes data obtained by both methods of observation.

In a previous paper,[2] in which qualitative effects of structure on burning velocity were discussed it was concluded that burning velocity increases in the order alkanes < alkenes < alkadienes with isolated double bonds ≅ alkadienes with conjugated double bonds < alkadienes with cumulated double bonds ≅ alkynes. These conclusions are supported in the present work. The effect of chain length on burning velocity is summarized in Fig. 1, wherein the solid lines represent previously published data,[1,2,10] and dashed lines connecting the solid lines to the symbols represent the trends found in the present work. It also has been found that methyl substitution decreases burning velocity, the extent of the decrease increasing with unsaturation.[2] The data in Table II show agreement with this latter generalization. In Fig. 2, burning velocity is plotted against side chain substituent for ring compounds. The solid lines connect members of the same ring series. As in the open chain hydrocarbons, burning velocity decreases with increasing extent of substitution. With somewhat less generality, it is seen that burning velocity decreases with increasing ring size. Previous work[2] indicates that unsaturation in the ring nucleus increases burning velocity. The trend in the aromatic series from the methyl to the butyl substituent is estimated on the basis of the general behavior of the ring compounds. The reason for the reversal of the expected relative positions of

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(9) P. L. Walker, Jr., and C. C. Wright, THIS JOURNAL, **74**, 3769 (1952).

(10) O. Levine and M. Gerstein, National Advisory Committee for Aeronautics RM E51J05, 1951.

TABLE I

BURNING VELOCITIES MEASURED BY THE BURNER METHOD

Name	T_1, °K.	T_2, °K.	$u_f(T_1)$, cm./sec.	$v_f(T_2)$, cm./sec.	a	c	$u_f(298)$, cm./sec.
n-Decane	367	422	57.0	72.0	1.67	2.97×10^{-3}	40.2
1-Decene	367	422	60.9	79.4	1.90	8.20×10^{-4}	41.2
Hexadecane	..	451	..	82.3	1.70[a]	2.53×10^{-3}	40.7
Benzene	311	395	48.2	73.8	1.78	1.76×10^{-3}	44.6
Toluene	318	422	42.5	63.8	1.43	1.12×10^{-2}	38.8
o-Xylene	367	422	47.5	59.0	1.55	5.03×10^{-3}	34.4
1,2,4-Trimethylbenzene	367	422	45.5	55.0	1.36	1.48×10^{-2}	34.3
n-Butylbenzene	367	422	54.0	71.0	1.96	5.07×10^{-4}	35.9
t-Butylbenzene	367	422	55.0	72.3	1.96	5.18×10^{-4}	36.9
Diphenylmethane	..	448	..	69.5	1.80[a]	1.17×10^{-3}	33.2
Tetralin	378	422	55.0	66.8	1.76	1.60×10^{-3}	36.2
trans-Decalin	367	422	51.2	67.5	1.98	4.28×10^{-3}	33.9

[a] Estimated average value for the particular class of compound.

TABLE II

COMPARISON OF MEASURED AND CALCULATED BURNING VELOCITIES

Name	ϕ[a]	T_f, °K.	P_H, atm. $\times 10^3$	P_{OH}, atm. $\times 10^3$	P_O, atm. $\times 10^3$	u_f(th.) cm./sec.	u_f(exp.) cm./sec.
Propadiene	1.21	2463	2.608	3.023	0.427	67.5	73.8
2-Methylpropane[b]	1.10	..	...	...	...	..	34.9
1-Deutero-2-methylpropane	1.10	..	...	...	...	..	33.4
2-Deutero-2-methylpropane	1.10	..	...	...	...	..	33.4
1-Butene-3-yne	1.09	2510	1.919	5.044	1.454	60.7	75.5
2,3-Dimethyl-1-butene	1.31	2206	0.889	0.610	0.020	38.6	39.2
2,3-Dimethyl-2-butene[c]	1.15	2284	.939	1.517	.109	39.8	37.2
2-Pentene	1.24	2242	.995	0.858	.038	41.1	43.1
2-Pentyne[c]	1.15	2378	1.402	2.603	.318	50.6	51.3
4-Methyl-2-pentyne	1.25	2311	1.356	1.293	.085	45.8	45.6
2-Methyl-1,3-pentadiene[c]	1.15	2345	1.205	2.149	.217	44.7	39.0
Methylcyclopropane	1.16	2319	1.169	1.845	.152	45.9	49.2
Ethylcyclopropane	1.25	2291	1.199	1.306	.080	45.9	47.5
cis-1,2-Dimethylcyclopropane	1.16	2319	1.022	2.114	.200	45.8	46.5
trans-1,2-Dimethylcyclopropane	1.18	2312	1.052	1.900	.163	44.9	46.2
1,1,2-Trimethylcyclopropane	1.15	2310	0.972	2.004	.183	43.3	43.5
2-Cyclopropyl-1-butene[c]	1.15	2342	1.193	2.128	.215	45.9	42.5
Cyclobutane	1.15	2311	1.086	1.817	.149	51.3	56.6
Ethylcyclobutane[c]	1.15	2291	0.975	1.589	.012	42.2	44.7
Isopropylcyclobutane	1.35	2168	.787	0.412	.010	37.1	39.1
n-Decane[d]	1.05	2287	.635	2.416	.266	39.2	40.2
1-Decene[d]	1.12	2298	.895	1.841	.158	41.1	41.2
Hexadecane[d]	1.08	2284	.727	2.030	.191	39.5	40.7
Benzene[d]	1.08	2362	.820	2.580	.459	41.2	44.6
Toluene[d]	1.05	2343	.698	2.700	.472	39.6	38.8
o-Xylene[d]	1.08	2337	.789	2.421	.354	39.8	34.4
1,2,4-Trimethylbenzene[d]	1.09	2324	.778	2.212	.287	39.1	34.3
n-Butylbenzene[d]	1.08	2327	.782	2.353	.314	39.8	35.9
t-Butylbenzene[d]	1.05	2321	.664	2.558	.379	39.2	36.6
Diphenylmethane[d]	1.07	2351	.722	2.446	.448	39.2	33.2
Tetralin[d]	1.01	2319	.519	2.779	.515	37.7	36.2
trans-Decalin[d]	1.09	2290	.729	1.955	.193	38.0	33.9
Dimethyl ether	1.19	2228	.878	1.160	.050	46.2	45.6
Diethyl ether	1.15	2254	.851	1.423	.083	42.2	39.9
Ethylene oxide	1.25	2411	2.257	3.090	.316	77.2	91.3
1,2-Propylene oxide	1.28	2317	1.553	1.503	.092	61.8	69.7
Propionaldehyde	1.31	2141	0.634	0.400	.009	40.1	49.0
Acetone	1.31	2123	.571	.346	.007	37.8	45.5
Acrylonitrile[d]	1.05	2461	1.327	4.410	1.207	56.5	47.0
Isopropylamine	1.14	2241	0.841	1.245	0.064	36.1	26.7

[a] ϕ = fuel/air at maximum u_f divided by fuel/air at stoichiometric. [b] From reference 1. [c] Composition for maximum u_f taken at ϕ = 1.15. [d] These compounds were measured in the Bunsen burner.

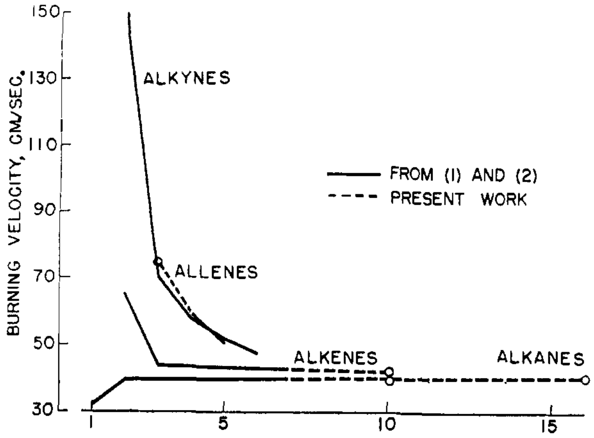

Fig. 1.—Burning velocity trends in straight-chain hydrocarbons.

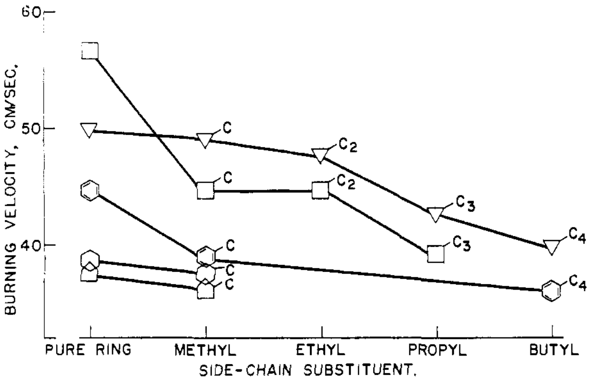

Fig. 2.—Burning velocity trends in cyclic hydrocarbons, effects of ring size and substitution.

cyclobutane and cyclopropane is not obvious at this time.

NOTE ADDED IN PROOF.—Since cyclopropane isomerizes to propylene at elevated temperatures, the possibility that this process is preceding the combustion process has been considered. Considering the temperature change in the initial mixture as cyclopropane → propylene + heat, and then computing the burning velocity of the preheated propylene mixture (taking the temperature dependence as $T_0^{1.7}$) the calculated burning velocity corresponds exactly to that measured for cyclopropane. Therefore, it must be considered that the reported burning velocity for cyclopropane and its consequent anomalous behavior compared with cyclobutane may in actuality be the burning velocity of propylene at an elevated temperature.

The oxygen- and nitrogen-containing compounds have not been studied extensively enough to permit a general formulation of their burning velocity trends. From the information included in this work, it would appear that the introduction of an oxygen atom into a molecule tends to increase the burning velocity, while introduction of a nitrogen atom seems to decrease the burning velocity. The oxygenated compounds exhibit a decreasing burning velocity as the oxygen linkage progresses from the epoxy to the carbonyl to the ether linkage.[11] In addition, increasing the length of the chain appears to decrease the normal burning velocity in the same manner as is observed in the pure hydrocarbon case.

The burning velocities of 1-deutero-2-methylpropane and 2-deutero-2-methylpropane[12] are reported. The measured burning velocities along with that of 2-methylpropane are listed in Table II. The effect of deuteration, while quite small, is in the direction consistent with either a diffusion or thermal concept of the flame propagation process.

Burning velocities for the compounds reported here have been calculated in a manner essentially the same as that described by Simon.[6]

The modified Tanford–Pease equation[6] used for these calculations is written

$$u_t = \left[nL\,\frac{Q'}{Q}\left(\frac{p_{\mathrm{H}}D_{\mathrm{H}}}{B_{\mathrm{H}}} + p_{\mathrm{OH}}D_{\mathrm{OH}} + p_{\mathrm{O}}D_{\mathrm{O}}\right)k_{\mathrm{av}}\right]^{1/2} \quad (5)$$

where

H, OH, and O refer to hydrogen, hydroxyl and oxygen radicals, respectively

p = mole fraction of the appropriate particle (or radical) at equilibrium flame temp. expressed as the partial pressure
D = diffusion coefficient of the active particle
B = radical recombination factor for the active particle
k_{av} = average over-all rate constant for reactions of active particles with fuel
L = molecules per cubic centimeter of gas at flame temperature[13]
Q' = initial mole fraction of combustible
Q = mole fraction of potential combustion product

Computation of equilibrium flame temperatures and active particle concentrations requires information on the heats of combustion of the compounds. These heats of combustion are derived in the computing process from the standard heat of formation. However, there is no single self-consistent set of data which includes the standard heats of formation of all the compounds considered in this paper. In order to insure self consistency, heats of formation at 298°K. were calculated by the incremental method of Franklin.[15] The calculated values for the heats of formation and heats of combustion were compared wherever possible with published values. In no case did there appear to be a discrepancy which

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[11] The burning velocity data of Experiment, Inc., as reported by Calcote, Barnett and Irby, in a paper presented at the 116th Meeting of the American Chemical Society, Atlantic City, N. J., are not in agreement with these suggested trends. In the data of Calcote, *et al.*, the relative positions of diethyl ether and propionaldehyde, and of acetone and propane are reversed as compared to the burning velocity values being reported here.

[12] We wish to thank Dr. C. E. Boord of Ohio State University for preparing these compounds for this work.

[13] This particular definition of L is not necessarily unique. In the original derivation[14] of the Tanford–Pease equation, it is assumed that all of the combustion zone is at a constant mean temperature, T_{m}, where $T_{\mathrm{m}} = 0.7T_{\mathrm{flame}}$. It is further assumed that in the process of heating the reactants from the initial temperature T_0 to the temperature T_{m}, some reaction takes place. The extent of the reaction is chosen so that the number of fuel molecules per cubic centimeter which are unreacted in the combustion zone is given by

$$Q'L = 0.7Q'L_0(T_0/T_{\mathrm{m}})$$

where L_0 is the number of fuel molecules per cubic centimeter at the initial condition. Upon substitution for T_{m}, it is seen that L is actually the number of fuel molecules per cubic centimeter at flame temperature, as defined in the text.

However, it should be noted that if the fraction of molecules which remains unreacted upon entering the combustion zone is not chosen to be seven-tenths of the initial value, then the value of L will be defined by the appropriate fraction of the flame temperature concentration. In the present case, where an empirical constant is to be employed, any manipulation of either the concentration term, L, or the mean temperature, T_{m}, would merely be reflected in a revised value of the empirical rate constant. The present definitions were chosen to maintain consistency with previous papers in this series.

[14] C. Tanford and R. N. Pease, *J. Chem. Phys.*, **15**, 433 (1947).

[15] J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1071 (1949).

could affect the calculated flame temperature by more than 5°, which is of the order of one-fourth of one per cent. Equilibrium flame temperatures and active particle concentrations were calculated by the matrix method of Huff and Morrell.[16] The results of these calculations are listed in Table II. Simon[6] used a value of k_{av} equal to 2.56×10^{-13} ml. molecule^{-1} sec.$^{-1}$ calculated from 56 hydrocarbon burning velocities.[17] Inclusion of the present hydrocarbon data into the averaging process yields $k_{av} = 2.57 \times 10^{-13}$ ml. molecule^{-1} sec.$^{-1}$ for a total of 85 compounds. This constant was used for all the burning velocity calculations.

Calculated and measured burning velocities are tabulated in Table II. Also included in the table are the calculated equilibrium flame temperatures, active particle concentrations and the initial mixture compositions for which the calculations were made.

A comparison of the calculated and measured values of the burning velocities (Table II) shows that for the twenty-nine hydrocarbon compounds for which burning velocities have been calculated, twenty-three are within 10% of the measured value, five between 10 and 15%, and only 1-butene-3-yne differs by more than 15%. For the oxygen and nitrogen substituted compounds, two of the eight calculated burning velocities fall within 10% of the measured burning velocity while the remaining six compounds deviate by larger values. The calculated burning velocities for the oxygenated compounds were all too low (except for the ethers), while calculations for the two nitrogenated compounds gave values which were in excess of the measured values. In view of the fact that these data represent wide variations in molecular structure and method of measurement, and that k_{av} was originally determined from hydrocarbon data only, it is felt that the agreement is satisfactory. The comparison would look even better if a different constant, $k_{av} = 3.21 \times 10^{-13}$ ml. molecules^{-1} sec.$^{-1}$, had been used to calculate the burning velocity of the six oxygen-containing compounds.

Burning velocities computed by the empirical method of Hibbard and Pinkel[18] were compared with measured values. While only about half of the hydrocarbons considered here could be computed by this method, the available results suggest that although fewer compounds may be considered without further experimental work, this method of computation is about as accurate as the Simon[6] method.

Figure 3 is a burning velocity–relative active particle concentration correlation of the type first used by Linnett and Hoare.[19] The dashed line is the correlation of Simon[6] for 56 pure hydrocarbons in air. It is seen that the majority of the present hydrocarbon data fall on or very near the correlation, while the largest portion of the remaining compounds deviate very markedly.

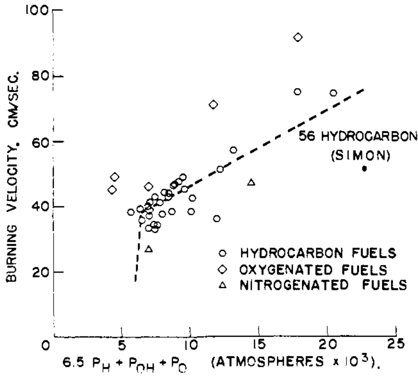

Fig. 3.—Comparison of burning velocity and relative active particle concentration with previous correlation.

It has been suggested[6] that if the use of an over-all rate constant (k_{av}) is meaningful in discussing the mechanism of hydrocarbon combustion, then the mechanism must be very much the same for all hydrocarbons except ethylene and acetylene. Figure 3 shows that almost all the hydrocarbon data are correlated as would be expected for a situation where the mechanism is similar. The major exception is 1-butene-3-yne, and since this compound bears a marked relation to the structures of both ethylene and acetylene, the observation regarding the anomalous behavior of those compounds appears to be borne out. The calculated relative atom concentrations for the oxygen-containing, and the nitrogen-containing compounds fall off the correlation. Following the same line of reasoning as was used for the hydrocarbon case, it would appear that for these compounds the combustion in air proceeds by some different mechanism (or mechanisms) than that for the hydrocarbons.

Acknowledgment.—The authors wish to thank Dr. M. Gerstein, Dr. E. A. Fletcher, Mr. E. L. Wong, Mr. O. Levine and Mrs. D. D. Graab for their assistance in the preparation of this work.

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[16] V. N. Huff and V. Morrell, National Advisory Committee for Aeronautics, TN 2113, 1950.

[17] Originally, the reported value of k_{av} was 2.33×10^{-13} ml. molecule^{-1} sec.$^{-1}$. This value was in error due to a numerical mistake made in the original computations. The corrected value appears in this text.

[18] R. R. Hibbard and B. Pinkel, THIS JOURNAL, **73**, 1622 (1951).

[19] J. W. Linnett and M. F. Hoare, "Third Symposium on Combustion, Flame and Explosion Phenomena," Williams and Wilkins, Baltimore, Maryland, 1949, p. 195.