reduce the speed of the hydrazine-destroying reaction and thus to favor the slower hydrazine-producing process. In the anhydrous system the ammonia functions not only as reactant but also as solvent. A comparison of the data in Table III with those in Table II indicate that the principal effect of the large excess of ammonia is operative in the liquid condensate in trap I rather than in the gaseous reaction tube. We believe, therefore, that the excess of ammonia functions as a diluent for the chloroamine, hydrazine, and ammonium ion. According to this hypothesis, we should not be surprised that in the anhydrous system an even higher ammonia to chlorine ratio is required for a good yield of hydrazine than in the aqueous Raschig synthesis.

Research toward the more complete understanding of the nature of this reaction and toward the improvement of the yield of hydrazine is being continued in this laboratory.

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

# Flame Propagation. IV. Correlation of Maximum Fundamental Flame Velocity with Hydrocarbon Structure

BY R. R. HIBBARD AND B. PINKEL

A correlation has been developed between the maximum fundamental flame velocity of hydrocarbons burning in air and the structure of the hydrocarbon. This maximum velocity appears to be a function of the concentrations of the various types of carbon–hydrogen bonds in the inflammable mixture. Maximum flame velocities can be calculated from an equation of the type: flame velocity $= N_AK_A + N_BK_C + N_CK_C \ldots$ where $N_A$, $N_B$, $N_C \ldots$ are the concentrations of the various types of C–H bonds and $K_A$, $K_B$, $K_C \ldots$ are empirically derived flame speed coefficients. Maximum flame velocities have been calculated for 34 hydrocarbons and compared with experimentally observed values. The average difference between calculated and observed flame velocity is less than 2% if one hydrocarbon is omitted from the average and the derived coefficients line up in approximately the order expected from other chemical considerations.

## Introduction

A study has been made of the flame speed data of Gerstein, Levine and Wong[1] in an attempt to determine what elements of hydrocarbon structure might account for the observed variations in flame speed. It was hoped that some relationship could be established between flame speed and structure which would permit the estimation of flame speeds for any hydrocarbon and eliminate the necessity for the experimental determination of this property.

Preliminary work showed little promise in attempts to correlate the concentrations of the various types of carbon–carbon bonds with maximum fundamental flame velocity ($U_f$). However, it was found that a reasonably accurate prediction of $U_f$ could be made on the basis of the concentrations of the various types of carbon–hydrogen bonds in the hydrocarbon molecule. An empirical equation is proposed which gives $U_f$ as a function of the concentrations of the various types of C–H bonds and parameters expressing the contribution of each type of C–H bond to $U_f$.

The values for these flame speed parameters are determined from the experimental data of Gerstein, *et al.* The equation is then used to calculate $U_f$ for 34 hydrocarbons and a comparison is made of the calculated and experimental values. While it appears that the rate of burning can be predicted from the concentrations of the various types of C–H bonds, no attempt is made, herein, to propose an oxidation mechanism and the results are presented on an empirical basis only.

## Analysis

It was assumed, in this study, that $U_f$ was dependent on all of the various types of C–H bonds in the hydrocarbon molecule and that each of these types had associated with it a different flame speed coefficient which represented the contribution of this type bond to the net flame speed. The simplest equation which would represent the contribution of each type of C–H bond to $U_f$ is an additive function of the product of the concentration of each type of bond times the corresponding flame speed coefficient, such as

$$U_f = N_AK_A + N_BK_B + N_CK_C \ldots \quad (1)$$

where $N_A$, $N_B$, $N_C \ldots$ are the numbers of the various types of C–H bonds per unit volume of hydrocarbon–air mixture, and $K_A$, $K_B$, $K_C, \ldots$, are the flame speed coefficients of these bonds.

Equation (1) assumes that the contribution of each type of C–H bond to $U_f$ is not influenced by other bonding effects in the carbon skeleton of the hydrocarbon. While this appears to be true as a first approximation for alkanes and alkenes, there appears to be a considerable effect by the alkyne C≡C bond on these C–H bonds which are on carbon atoms situated alpha to the C≡C. This effect is introduced into the equation by means of a factor, $M$, which introduces terms which augment the contribution of those C–H bonds which are on carbon atoms placed alpha to the C≡C bond. The equation then is modified to read

$$U_f = N_AK_A + N_BK_B + N_CK_C \ldots + MN_{B\alpha}K_B + MN_{C\alpha}K_C \quad (2)$$

where $M$ is the activation factor for alpha placed

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

C–H bonds, and $N_{B\alpha}$, $N_{C\alpha}$ are the number of B or C type C–H bonds on carbon atoms alpha to the $C{\equiv}C$.

Throughout this report $N_A$, $N_B$, $N_C$, $N_D$, $N_E$, $N_F$, $N_G$ and $N_H$ are the numbers of methane, primary, secondary, tertiary, alkene, alkyne, cyclohexyl and aromatic C–H bonds, respectively, per ml. of hydrocarbon–air mixture and $K_A$, $K_B$, $K_C$,..., are the corresponding flame speed coefficients for these bonds. $M$ is the influence factor for bonds on carbon atoms which are alpha to $C{\equiv}C$ and $N_{B\alpha}$ and $N_{C\alpha}$ are the numbers of primary and secondary C–H bonds on carbon atoms alpha to $C{\equiv}C$.

**Evaluation of Coefficients.**—Table I presents for 37 hydrocarbons the maximum flame velocity $U_f$ in column (1), and the per cent. hydrocarbon in the mixture giving $U_f$ in column (2), both taken from Gerstein. In column (3) of Table I are the hydrocarbon to air weight ratios at the conditions for $U_f$.

TABLE I

MAXIMUM FUNDAMENTAL FLAME VELOCITIES AND CONCENTRATIONS OF HYDROCARBON–AIR MIXTURES

| | | Concentrations for mixtures giving maximum flame velocity | | | |
|---|---|---|---|---|---|
| Hydrocarbon | Maximum flame velocity $U_f$ cm./sec. exptl. data | Hydrocarbon, % by volume exptl. data | Hydrocarbon–air weight ratio exptl. data | Hydrocarbon–air weight ratio smoothed data | Number molecules per ml. smoothed data |
| Methane | 33.8 | 9.96 | 0.0612 | 0.0612[a] | 240 × $10^{16}$ |
| Ethane | 40.1 | 6.28 | .0696 | .0703 | 153 |
| Propane | 39.0 | 4.54 | .0724 | .0719 | 109 |
| Butane | 37.9 | 3.52 | .0732 | .0735 | 85.3 |
| Pentane | 38.5 | 2.92 | .0748 | .0752 | 70.7 |
| Hexane | 38.5 | 2.51 | .0764 | .0768 | 60.7 |
| Heptane | 38.6 | 2.26 | .0798 | .0784 | 53.5 |
| 2-Methylpropane | 34.9 | 3.48 | .0724 | .0722 | 83.8 |
| 2,2-Dimethylpropane | 33.3 | 2.85 | .0730 | .0729 | 68.6 |
| 2-Methylbutane | 36.6 | 2.89 | .0740 | .0738 | 69.5 |
| 2,2-Dimethylbutane | 35.7 | 2.43 | .0740 | .0746 | 59.0 |
| 2,3-Dimethylbutane | 36.3 | 2.45 | .0746 | .0746 | 59.0 |
| 2,2,3-Trimethylbutane | 35.9 | 2.15 | .0760 | .0763 | 52.1 |
| 2-Methylpentane | 36.8 | 2.46 | .0750 | .0755 | 59.7 |
| 3-Methylpentane | 36.7 | 2.48 | .0756 | .0755 | 59.7 |
| 2,3-Dimethylpentane | 36.5 | 2.22 | .0784 | .0763 | 52.1 |
| 2,4-Dimethylpentane | 35.7 | 2.17 | .0767 | .0763 | 52.1 |
| Ethene | 68.3 | 7.40 | .0773 | .0761 | 176 |
| Propene | 43.8 | 5.04 | .0770 | .0769 | 121 |
| 1-Butene | 43.2 | 3.87 | .0780 | .0777 | 93.1 |
| 1-Pentene | 42.6 | 3.07 | .0766 | .0785 | 75.8 |
| 1-Hexene | 42.1 | 2.67 | .0796 | .0793 | 64.1 |
| 2-Methylpropene | 37.5 | 3.83 | .0770 | .0770 | 92.3 |
| 2-Methyl-1-butene | 39.0 | 3.12 | .0780 | .0778 | 75.1 |
| 2-Methyl-1-butene | 41.5 | 3.11 | .0776 | .0778 | 75.1 |
| 2-Ethyl-1-butene | 39.3 | 2.65 | .0790 | .0786 | 63.6 |
| 2-Methyl-1-pentene | 39.6 | 2.80 | .0838 | .0786 | 63.6 |
| 4-Methyl-1-pentene | 40.5 | 2.62 | .0780 | .0786 | 63.6 |
| Propyne | 69.9 | 5.86 | .0860 | .0854 | 140 |
| 1-Butyne | 58.1 | 4.36 | .0850 | .0856 | 106 |
| 1-Pentyne | 52.9 | 3.51 | .0854 | .0859 | 85.0 |
| 1-Hexyne | 48.5 | 2.97 | .0866 | .0861 | 71.1 |
| 4-Methyl-1-pentyne | 45.0 | 2.87 | .0836 | .0836 | 69.1 |
| 2-Butyne | 51.5 | 4.36 | .0850 | .0856 | 106 |
| 3-Hexyne | 45.4 | 3.50 | .0890 | .0861 | 71.1 |
| Cyclohexane | 38.7 | 2.65 | .0790 | .0790[a] | 63.9 |
| Benzene | 40.7 | 3.34 | .0930 | .0930[a] | 80.5 |

[a] Experimental values.

For the purpose of smoothing out experimental inaccuracies in the determination of the hydrocarbon concentration for maximum flame velocity, and to provide a basis for estimating $U_f$ in the absence of any experimental data, the hydrocarbon to air weight ratios were plotted against the number of carbon atoms in the hydrocarbon. Straight lines were drawn through the points for each class of hydrocarbon and are shown as Fig. 1. From this figure were estimated the hydrocarbon to air weight ratios for maximum flame velocities and these values are listed in column (4) of Table I. The flame speed coefficients were all calculated from the smoothed data except for methane, cyclohexane and benzene where the experimentally observed hydrocarbon concentrations were used.

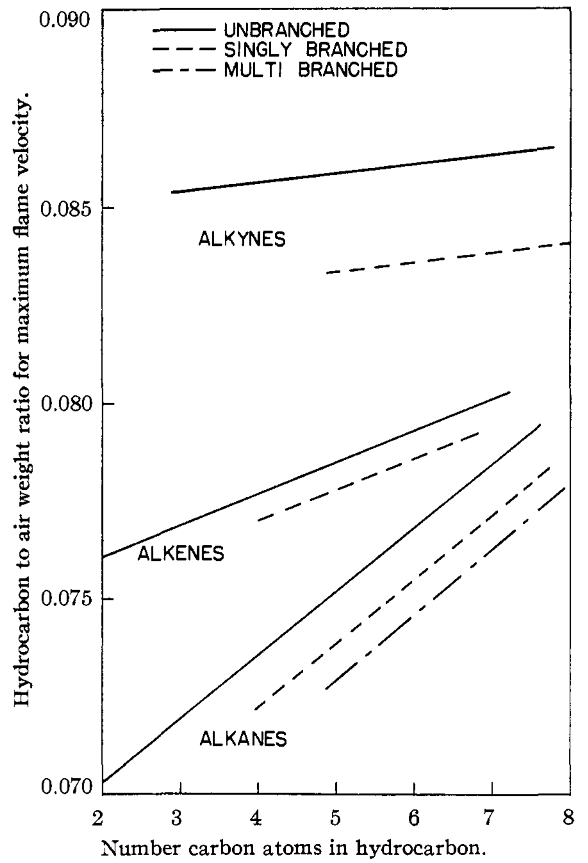

Fig. 1.—Hydrocarbon concentrations for maximum flame velocity.

Also shown in Table I in column (5) are the numbers of hydrocarbon molecules per ml. of hydrocarbon–air mixture for the concentrations given in column (4). These values were calculated at the approximately average laboratory conditions of flame speed measurement of 298°K. and 745 mm. pressure assuming perfect gases. From the number of hydrocarbon molecules per ml. were calculated the numbers of the various types of C–H bonds per ml. ($N_A$, $N_B$, $N_C$,...).

For the evaluation of the methane, cyclohexyl and aromatic flame speed coefficients, data were available for only one hydrocarbon of each class (methane, cyclohexane, benzene) and each hydrocarbon contained only a single type of C–H bond. These coefficients were calculated by simply dividing the different values for $U_f$ by $N_A$, $N_G$, and $N_H$. The resulting coefficients are

$$K_A \text{ (methane)} = 35.2 \times 10^{-19}$$
$$K_G \text{ (cyclohexyl)} = 50.5 \times 10^{-19}$$
$$K_H \text{ (aromatic)} = 84.3 \times 10^{-19}$$

For the balance of the paraffins the coefficients $K_B$, $K_C$, and $K_D$ were evaluated by the application of least squares to the equation

$$U_f = N_BK_B + N_CK_C + N_DK_D \qquad (3)$$

using the data for all the paraffins except methane. The values so derived are

$$K_B \text{ (primary)} = 42.5 \times 10^{-19}$$
$$K_C \text{ (secondary)} = 47.5 \times 10^{-19}$$
$$K_D \text{ (tertiary)} = 45.4 \times 10^{-19}$$

Using the above values for $K_B$, $K_C$, and $K_D$, the alkene flame speed coefficient, $K_E$, was evaluated by least squares in the equation

$$U_f = N_BK_B + N_CK_C + N_DK_D + N_EK_E \qquad (4)$$

using all the alkene data except that for ethene. This first member of the series was omitted because preliminary calculations had shown it to require a very much higher value for $K_E$ than did the other alkenes. The flame speed coefficient, $K_E$, was found to be $80.7 \times 10^{-19}$.

For the alkyne series and again using the previously established values for $K_B$ and $K_C$, the influence factor, $M$, was established from the data for 2-butyne and 3-hexyne. $M$ was the average of the values required to give perfect agreement between the experimental values for $U_f$ and those calculated from equation (2) for these two compounds. This influence factor, $M$, had an average value of 0.96 and since this effect is presumably present in alkynes with both terminal and internal triple bonds, this factor was applied to all the alkyne data and the coefficient $K_F$ found to be 223.9 $\times 10^{-19}$.

The values for all the coefficients in equation (2) are listed in Table II for easy comparison. The flame speed coefficients are listed in order of increasing numerical values and show the alkane C–H bonds to be the lowest, the alkyne C–H bond to be the highest, and the alkene and aromatic bonds to be intermediate in their effect on $U_f$.

TABLE II

COEFFICIENTS FOR CALCULATING MAXIMUM FLAME VELOCITY

| Type C-H bond | | Coefficient |
|---|---|---|
| Methane | $(K_A)$ | $35.2 \times 10^{-19}$ |
| Primary | $(K_B)$ | 42.5 |
| Secondary | $(K_C)$ | 47.5 |
| Tertiary | $(K_D)$ | 45.4 |
| Cyclohexyl | $(K_G)$ | 50.5 |
| Alkene | $(K_E)$ | 80.7 |
| Aromatic | $(K_H)$ | 84.3 |
| Alkyne | $(K_F)$ | 223.9 |
| Alpha coefficient | $(M)$ | 0.96 |

**Prediction of Maximum Uniform Flame Velocity.**—With values for $N_B$, $N_C$, . . ., calculated from the smoothed data taken from column (5) of Table I, and using the coefficients from Table II, $U_f$ was calculated for 34 hydrocarbons and compared with the experimental values in Table III. Methane, benzene and cyclohexane are omitted from this table since each is the only member of its class and the coefficients were calculated to give perfect agreement between experimental and predicted $U_f$ for each of these hydrocarbons.

## Discussion

The usefulness of equation (2) and the coefficients listed in Table II in predicting maximum flame speeds can be judged by a comparison of the calculated and experimentally determined values for $U_f$ shown in Table III. For the alkanes the differences are less than 3% for all but one of the hydrocarbons. Equally good results are shown for the alkenes with the exception of ethene which has a much higher $U_f$ than that predicted by equation (2). Simon,[2] in relating the $U_f$ of hydrocarbons with the concentration of active particles in the

TABLE III

COMPARISON OF CALCULATED AND OBSERVED MAXIMUM FLAME VELOCITIES

| Hydrocarbon | Max. flame velocity (cm./sec.) Exptl. | Calcd. | Δ | Difference, % |
|---|---|---|---|---|
| Ethane | 40.1 | 39.0 | −1.1 | 2.7 |
| Propane | 39.0 | 38.1 | −0.9 | 2.3 |
| Butane | 37.9 | 38.0 | 0.1 | 0.3 |
| Pentane | 38.5 | 38.2 | −0.3 | 0.8 |
| Hexane | 38.5 | 38.6 | 0.1 | 0.3 |
| Heptane | 38.6 | 39.0 | 0.4 | 1.0 |
| 2-Methylpropane | 34.9 | 35.9 | 1.0 | 2.9 |
| 2,2-Dimethylpropane | 33.3 | 35.0 | 1.7 | 5.1 |
| 2-Methylbutane | 36.6 | 36.3 | −0.3 | 0.8 |
| 2,2-Dimethylbutane | 35.7 | 35.7 | 0.0 | 0.0 |
| 2,3-Dimethylbutane | 36.3 | 35.5 | −0.8 | 2.2 |
| 2,2,3-Trimethylbutane | 35.9 | 35.6 | −0.3 | 0.8 |
| 2-Methylpentane | 36.8 | 36.9 | 0.1 | 0.3 |
| 3-Methylpentane | 36.7 | 36.9 | 0.2 | 0.5 |
| 2,3-Dimethylpentane | 36.5 | 36.3 | 0.2 | 0.5 |
| 2,4-Dimethylpentane | 35.7 | 36.3 | 0.6 | 1.7 |
| Average for alkanes | | | 0.51 | 1.39 |
| Ethene | 68.3 | 56.7 | −11.6 | 17.0 |
| Propene | 43.8 | 44.8 | 1.0 | 2.3 |
| 1-Butene | 43.2 | 43.2 | 0.0 | 0.0 |
| 1-Pentene | 42.6 | 42.4 | −0.2 | 0.5 |
| 1-Hexene | 42.1 | 42.0 | −0.1 | 0.2 |
| 2-Methylpropene | 37.5 | 38.5 | 1.0 | 2.7 |
| 2-Methyl-1-butene | 39.0 | 38.4 | −0.6 | 1.5 |
| 3-Methyl-1-butene | 41.5 | 40.8 | −0.7 | 1.7 |
| 2-Ethyl-1-butene | 39.3 | 38.6 | −0.7 | 1.8 |
| 2-Methyl-1-pentene | 39.6 | 38.6 | −1.0 | 2.5 |
| 4-Methyl-1-pentene | 40.5 | 40.5 | 0.0 | 0.0 |
| Average for alkenes | | | 1.54 | 2.74 |
| Average for alkenes, omitting ethene | | | 0.53 | 1.32 |
| Propyne | 69.9 | 66.6 | −3.3 | 4.7 |
| 1-Butyne | 58.1 | 56.9 | −1.2 | 2.1 |
| 1-Pentyne | 52.9 | 53.8 | 0.9 | 1.7 |
| 1-Hexyne | 48.5 | 51.7 | 3.2 | 6.6 |
| 4-Methyl-1-pentyne | 45.0 | 49.1 | 4.1 | 9.1 |
| 2-Butyne | 51.5 | 53.0 | 1.5 | 2.9 |
| 3-Hexyne | 45.4 | 44.7 | −0.7 | 1.5 |
| Average for alkynes | | | 2.13 | 4.08 |
| Average for all hydrocarbons | | | 1.17 | 2.38 |
| Average for all hydrocarbons, omitting ethene | | | 0.86 | 1.94 |

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[2] D. M. Simon, THIS JOURNAL, **73**, 422 (1951).

flame, observed a similar deviation for ethene with deviations for this hydrocarbon being about six times the average deviation for other hydrocarbons and with the observed $U_f$ also being much higher than the calculated $U_f$. The agreement between calculated and experimental $U_f$ for alkynes is somewhat poorer than for alkanes and alkenes. For all the hydrocarbons listed in Table III, the average difference between calculated and observed $U_f$ is 1.17 cm./sec. and 2.38%. If ethylene is omitted from the averages the average difference is 0.86 cm./sec. and 1.94%.

It must be admitted that the range of flame velocities covered in this study is relatively small and that the use of the many adjustable constants yields only a moderate increase in the accuracy of $U_f$ prediction over that which would be obtained by a simple statement that each of the various classes of hydrocarbons has, on the average, a single value for $U_f$. For example, the average $U_f$ for the alkanes, alkenes (omitting ethene) and alkynes listed in Table III are 36.9, 40.9 and 53.0 cm./sec., respectively. The average deviation between the experimental $U_f$ and the above average hydrocarbon class values is 2.51 cm./sec. for these compounds, or an inaccuracy of $U_f$ prediction only 2.9 times greater than that obtained by using equation (2). Therefore the increased accuracy in $U_f$ prediction obtained by use of equation (2) with its many adjustable constants over that which would be obtained by a simple statement of average hydrocarbon class flame velocities may not be of much statistical importance.

However, it does appear significant that the coefficients listed in Table II which were derived solely from flame velocity data line up in much the same order as would be expected from independent chemical considerations. The methane type C–H bond is the least reactive with the other alkane and cycloalkane bonds next in reactivity. The alkene and aromatic bonds both have values roughly twice those of the alkanes and the alkyne C–H group is by far the most reactive, having a coefficient about five times greater than the alkane bonds.

From chemical considerations the value for the tertiary C–H bond would have been expected to be higher than the secondary C–H bond. However, the tertiary C–H coefficient is the result of calculations based on a relatively small number of these bonds. In 1 ml. of hydrocarbon–air mixture of each of the 16 alkanes used to evaluate $K_B$, $K_C$, and $K_D$, there was a total of $99.2 \times 10^{18}$ primary C–H bonds, $29.5 \times 10^{18}$ secondary C–H bonds, and only $6.5 \times 10^{18}$ tertiary bonds. Therefore it is probable that the value for the tertiary coefficient is less reliable than for the other types of alkane bonds. Increasing the flame speed coefficient for the tertiary bond from $45.4 \times 10^{-19}$ to $50.0 \times 10^{-19}$ would increase the average calculated $U_f$ of the eight branched alkanes containing this group by only 0.37 cm./sec. and would have put this coefficient in the expected order relative to the other alkane values. The cyclohexane coefficient is the result of calculations on only one hydrocarbon and is open to question. The aromatic coefficient is also the result of calculations based on only one hydrocarbon but its value appears in a qualitatively correct position relative to the alkane and alkyne coefficients.

The alpha influence factor required for alkynes should have its counterpart in the alkene and aromatic series. For these series the value would be much closer to zero and the data are insufficiently precise to permit its evaluation for the alkenes. Data on substituted benzenes would be required to determine such a factor for the aromatic ring.

In general, it appears that the agreement between calculated and experimental maximum uniform flame velocities is too good, and the relative order of flame speed coefficients too reasonable to be a purely fortuitous correlation of data. However, no attempt is made to propose a kinetic mechanism for flame propagation based on this study.

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