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RESEARCH MEMORANDUM

FLAME VELOCITIES OF FOUR ALKYLSILANES

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and Oscar Levine

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RESEARCH MEMORANDUM

FLAME VELOCITIES OF FOUR ALKYLSILANES

By Melvin Gerstein, Edgar L. Wong

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SUMMARY

The rates of flame propagation of four alkylsilanes have been determined by a tube method. The maximum fundamental rate of flame propagation increases in the order: tetramethylsilane < trimethylsilane < diethylsilane < monoethylsilane. A precise fundamental flame velocity could not be obtained for monoethylsilane because of the high rate of propagation. In each case the alkylsilanes have considerably higher flame velocities than the hydrocarbons that would result if the silicon were replaced by carbon; whereas the physical properties of the alkylsilanes resemble those of the corresponding hydrocarbons. On the basis of a qualitative comparison, it appears that the mechanism of the chemical reaction may be important in determining the rate of flame propagation.

When diethylsilane is blended with n-pentane, no marked increase in flame velocity occurs until the concentration of diethylsilane is greater than 20 percent. The flame velocities of the blends are lower than would be predicted from a linear blending relation. At no concentration of total combustible does a mixture of diethylsilane and pentane have a higher flame velocity than diethylsilane at a concentration equal to the concentration of total combustible.

INTRODUCTION

The high-velocity combustion required in modern jet-propelled aircraft has revived interest in the study of fundamental combustion properties such as flame velocity, ignition energy, and flammability limits. The flame-velocity measurements of four alkylsilanes discussed in this report were directed towards finding fuels capable of supporting stable combustion in a high-velocity air stream and yet possessing physical properties similar to those of conventional fuels. The class of compounds being investigated, the alkylsilanes, was chosen after an examination of the literature because of the similarity of their physical properties to hydrocarbons and the indications that they might have high flame velocities.

Previous work by the authors (references 1 and 2) indicated that the majority of the hydrocarbons have flame velocities between 30 and 70 centimeters per second. Other investigators (reference 3) show that the maximum to be expected from organic compounds containing oxygen or nitrogen is about 90 centimeters per second. Although other exceptions may exist, only acetylene with a flame velocity of 157 centimeters per second and hydrogen with a flame velocity of 317 centimeters per second are notably higher. Unfortunately, acetylene because of its low boiling point and instability when stored under pressure, and hydrogen because of its low boiling point and low density cannot be used in fuel systems of conventional design.

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It is well known that the presence of metal-to-carbon bonds as in metal alkyls, or metal-to-hydrogen bonds as in hydrides, often leads to spontaneous inflammability at room temperature. It is reasonable to expect, therefore, that the presence of certain metal-to-carbon and metal-to-hydrogen bonds in a molecule might result in flame velocities considerably greater than most hydrocarbons. At the same time it would be desirable to have a fuel that was not spontaneously inflammable. Only a few metal alkyls or hydrides can meet this requirement. A preliminary investigation of one of them, diborane, indicates that it does have an exceptionally high rate of flame propagation (references 4 and 5). Unfortunately, diborane also has a low boiling point and decomposes when stored at room temperature. A class of compounds that meet the foregoing requirements is the alkylsilanes which, unlike silane itself, do not ignite spontaneously on contact with air at room temperature, are relatively easy to prepare, and, for some members, have densities and boiling points in the same range as conventional hydrocarbon fuels (reference 6).

This report contains the results of an investigation of the flame velocities of four alkylsilanes: monoethylsilane, diethylsilane, trimethylsilane, and tetramethylsilane, determined by the tube method of reference 1.

APPARATUS

The apparatus and experimental technique used for the measurement of the flame velocities were the same as those described in reference 1. The flame tube consists of a horizontal, cylindrical, Pyrex tube with an inside diameter of 25 millimeters and a length of 57 centimeters. An 8-millimeter-diameter orifice was placed at the ignition end of the flame tube and a second orifice, 1.7 millimeters in diameter, was placed at the opposite end. A methyl alcohol flame was used as the source of ignition.

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The linear or observed spatial flame velocity U_o was measured at room temperature and atmospheric pressure by means of two photocells placed $6\frac{1}{8}$ inches apart and connected to an electronic timer. The fundamental flame velocity U_f was calculated by the equation (reference 1)

$$U_f = (U_o - U_g)(A_t/A_f) \tag{1}$$

where

U_f fundamental flame velocity (velocity component normal to any tangent to flame surface)

U_o linear observed flame velocity (spatial velocity)

U_g gas velocity ahead of flame

A_t cross-sectional area of flame tube

A_f flame surface area

The gas velocity U_g was calculated by the empirical equation from reference 1

$$U_g = 0.236\ U_o - 10.47\ \text{cm/sec} \tag{2}$$

Superposition of photographs of alkylsilane flames on photographs of hydrocarbon flames showed that the flame front was the same in shape and dimensions. Consequently, the surface area of the flame A_f was assumed to be equal to that found for hydrocarbon-air flames, 11.25 square centimeters (reference 1). The alkylsilane flame had a slightly longer tail but this was ignored in the area calculations.

After each run with an alkylsilane, a fine deposit of silicon dioxide was left on the tube. This deposit was cleaned out with a glass-wool swab after each run. To check the effect of the deposit, runs were made in clean tubes and in tubes coated with varying quantities of silicon dioxide. At no time was a difference found in the flame velocities. The reproducibility of the experimental procedure was confirmed by periodic testing of n-pentane during the investigation of the alkylsilanes. At no time did the linear flame velocity for n-pentane deviate more than 2 percent from its original value (reference 1). At least three determinations of the linear flame velocity were made for each mixture concentration studied. The flame velocities reported herein are average values and have a precision of ±2 percent for tetramethylsilane and trimethylsilane. The precision of the flame

velocities for diethylsilane is only ±4 percent because of the greater difficulty in determining the flame surface area of fast flames. A fundamental flame velocity could not be obtained for monoethylsilane because of the uncertainty in the flame shape due to the high rate of propagation.

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FUELS

The alkylsilanes used in this investigation were prepared at the Lewis laboratory by reduction of the corresponding chlorides by lithium aluminum hydride (reference 7). The compounds were distilled over lithium hydride and have a purity greater than 97 percent as determined by carbon and silicon analyses and freezing point. Some physical properties of the alkylsilanes are given in table I. Of the compounds reported herein, only diethylsilane and tetramethylsilane have boiling points above room temperature, and all the silanes have freezing points below -100° C. The specific gravity of the alkylsilanes is between 0.65 and 0.68. The physical properties of the silanes are compared in table I with those hydrocarbons that would result if the silicon were replaced by carbon.

The alkylsilanes used in this investigation could be handled in air without appreciable oxidation or hydrolysis. The compounds containing many silicon-to-hydrogen bonds such as monoethylsilane and diethylsilane have a tendency to hydrolyze when kept in contact with water for extended periods of time.

RESULTS AND DISCUSSION

Alkylsilane flame velocities. - The fundamental flame velocities of diethylsilane, trimethylsilane, and tetramethylsilane are plotted in figure 1 as a function of the ratio of the fuel concentration to the stoichiometric fuel concentration for combustion in air. Similar data for ethylsilane could not be obtained by the tube method because the spatial rate of flame propagation was so high that a smooth flame front could not be distinguished. The spatial velocity for a lean mixture, 95 percent of stoichiometric, was about 560 centimeters per second. This can be compared with acetylene which gave a maximum spatial velocity of about 600 centimeters per second in the same tube. In any attempts to obtain spatial rates of flame propagation for mixtures richer in ethylsilane, the orifice towards which the flame advanced was forcibly blown from the tube.

The curves in figure 1 for the other alkylsilanes resemble those obtained for hydrocarbons (references 1 and 2). In each case the

maximum flame velocity occurs slightly to the rich side of stoichiometric. The scatter of the points in the curve for diethylsilane indicates that a flame velocity of about 100 centimeters per second is near the limit of the present apparatus.

Maximum flame velocities taken from the curves of figure 1 are summarized in table I and plotted in figure 2. The maximum flame velocity increases rapidly as the number of silicon-to-hydrogen bonds is increased, although the alkyl groups attached to the silicon were not the same in all cases. Ethylsilane would fall considerably above diethylsilane, whereas silane (SiH_4), which has only silicon-to-hydrogen bonds, can be assumed to have infinite flame velocity because it is spontaneously inflammable at room temperature.

An intersting comparison can be made between diethylsilane and tetramethylsilane because they are isomers and, consequently, have the same products of combustion. Diethylsilane has a flame velocity about 100 percent greater than that of tetramethylsilane.

Blends of diethylsilane and n-pentane. - The use of the alkylsilanes as additives to petroleum fuels was considered as a possible means of increasing the rate of flame propagation of the fuel. The rate of flame propagation of mixtures of n-pentane and diethylsilane is shown in figure 3. The flame velocity is plotted against the fraction of diethylsilane in the fuel for constant over-all concentrations of fuel plus additive. Both pentane and diethylsilane have the same stoichiometric concentration on a volumetric basis. The curve for 2.94-percent total inflammable is near the concentration for maximum flame velocity for pure n-pentane and pure diethylsilane, and the other curves represent concentrations on either side of the maximum. The curves illustrate that there is no positive catalytic effect when diethylsilane is added to n-pentane. In fact, the first 20 percent of diethylsilane increases the flame velocity only about 10 percent. The flame velocities of the blends are lower than would be predicted from a linear blending relation. A cross-plot of the data as an additional illustration of the trends is given in figure 4, where the flame velocity is plotted against the total concentration of combustible (fuel and additive) for constant percentages of diethylsilane in the n-pentane. As expected, the flame velocity increases as the concentration of additive increases, with the maximum for each curve occurring in the vicinity of 3.0-percent total inflammable by volume.

Flame propagation theories. - The thermodynamic and kinetic data available for the alkylsilanes are still insufficient for application of theories of flame propagation. It is possible, however, to calculate heats of combustion using heats of formation obtained from bond energies

by the method of Pauling (reference 8). The results of these calculations are given in table I along with similar data for the hydrocarbons that would result if the silicon were replaced by carbon. A rough estimate of the accuracy of the calculated heats of combustion can be obtained for SiH_4. Bichowsky and Rossini (reference 9) report a heat of combustion of 324 kcal per mole; the calculated value is 326 kcal per mole.

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A striking point is that the heat of combustion of diethylsilane is only about 2 percent greater than that of tetramethylsilane, whereas the flame velocity of the diethylsilane is 100 percent greater as previously mentioned.

Two principal types of theory of flame propagation have been proposed: thermal theories in which heat conduction from the flame front is the rate-controlling step, and diffusion theories in which the diffusion of active particles from the flame front into the unburned gas is the rate-controlling step. Inasmuch as the heats of combustion of the two isomers are so nearly the same, the flame temperatures and, hence, the rate of heat conduction would also be alike. Similarly, because the active particle concentrations depend strongly on flame temperature, it is unlikely that there would be sufficient difference between the two isomers to account for the two-fold increase in flame velocity of diethylsilane over tetramethylsilane.

It appears, therefore, that other factors must be considered in the rate of flame propagation such as the ignition temperatures of the mixtures or the relative effectiveness of active particles in producing the flame reactions. In other words, the mechanism of the reaction may be important in determining the rate of flame propagation inasmuch as both the factors just mentioned are reflected in the oxidation mechanism.

The indication that the partial pressures and diffusion coefficients of some of the important free radicals are not sufficient to account for flame velocity variations is given by the deviation of ethylene from the correlation of hydrocarbon flame velocities by a diffusion theory (reference 10). Ethylene has a higher flame velocity than that predicted by the diffusion of free radicals unless a higher reaction-rate constant is used for ethylene than is used for most other hydrocarbons. Sachsse and Bartholomé (reference 11) show a similar deviation; for a curve of hydrogen atom concentration plotted against flame velocity, hydrogen and acetylene fall considerably above the curve for carbon monoxide and some saturated hydrocarbons.

The principal difference between diethylsilane and tetramethylsilane is that the former contains two silicon-to-hydrogen bonds,

whereas the latter contains none. It is possible, therefore, that the rate of reaction of oxygen or of some free radicals with the silicon-to-hydrogen bond as opposed to the rate of reaction of the same substances with carbon-to-hydrogen bonds is important in the propagation process. The importance of silicon-to-hydrogen bonds has already been indicated in the discussion of the data illustrated in figure 2.

A comparison can also be made between alkylsilanes and the hydrocarbons that result when the silicon is replaced by carbon. Inasmuch as the products of combustion are different, however, the results are more difficult to interpret. In each case the silane has a heat of combustion about 100 kcal per mole greater than the corresponding hydrocarbon. About 80 kcal per mole of this could be considered as being used to melt and vaporize SiO_2 so that it cannot be considered as contributing greatly to increased flame temperature or free radical concentrations. The resulting heats of combustion of the silanes, for gaseous SiO_2, are only from 0 to 10 percent greater than those of the corresponding hydrocarbons. Here, too, it is difficult to account for the extremely large difference in flame velocity, almost three-fold in the case of diethylsilane as compared with n-pentane, on this relatively small difference in heat of combustion. This comparison also strongly suggests the importance of the mechanism of the chemical reaction in the rate of flame propagation. The difference in reactivity of compounds containing silicon compared with hydrocarbons has been reported by many investigators for a variety of reactions. Rochow (reference 12) states that, although silicon remains tetravalent like carbon in its organic compounds, the presence of silicon in the molecule may cause vigorous reactions that are unknown in the analagous carbon compounds.

SUMMARY OF RESULTS

1. The rates of flame propagation of four alkylsilanes have been studied. The maximum rate of flame propagation increases in the order tetramethylsilane < trimethylsilane < diethylsilane < monoethylsilane.

2. In each case the alkylsilanes have a considerably higher flame velocity than the hydrocarbons that would result if the silicon were replaced by carbon. The physical properties of the alkylsilanes resemble those of the corresponding hydrocarbon.

3. On the basis of a qualitative comparison, it appears that the mechanism of the chemical reaction may be important in determining the rate of flame propagation through mixtures of alkylsilanes and air.

4. When diethylsilane is mixed with n-pentane, no marked increase in flame velocity occurs until the concentration of diethylsilane is

quite high. The flame velocities of the blends are lower than would be predicted by a linear blending relation.

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Cleveland, Ohio.

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REFERENCES

1. Gerstein, Melvin, Levine, Oscar, and Wong, Edgar L.: Fundamental Flame Velocities of Pure Hydrocarbons. I - Alkanes, Alkenes, Alkynes, Benzene, and Cyclohexane. NACA RM E50G24, 1950.

2. Levine, Oscar, Wong, Edgar L., and Gerstein, Melvin: Fundamental Flame Velocities of Pure Hydrocarbons. II - Alkadienes. NACA RM E50H25, 1950.

3. Calcote, Hartwell F., Barnett, Charles M., and Irby, Moreland R.: The Burning Velocity of Various Compounds by the Bunsen Burner Method. Paper presented at 116th Meeting of the Am. Chem. Soc., (Atlantic City, N. J.), Sept. 18-23, 1949. (See Abstracts of Papers 116th Meeting of Am. Chem. Soc., p. 38P.)

4. Gammon, Benson E., Genco, Russell S., and Gerstein, Melvin: A Preliminary Experimental and Analytical Evaluation of Diborane as a Ram-Jet Fuel. NACA RM E50J04, 1950.

5. Price, F. P.: Burning and Detonation of Mixtures of Boron Hydrides with Air and Oxygen. Rep. No. R50A0504, Apparatus Dept., Gen. Elec. Co., March 1950. (Proj. HERMES, Ord. Dept.)

6. Finholt, A. E., Bond, A. C., Jr., Wilzbach, K. E., and Schlesinger, H. I.: The Preparation and Some Properties of Hydrides of Elements of the Fourth Group of the Periodic System and of their Organic Derivatives. Jour. Am. Chem. Soc., vol. 69, no. 11, Nov. 1947, pp. 2692-2696.

7. Tannenbaum, Stanley, and Murphy, Maurice F.: The Preparation, Physical Properties, and Heats of Combustion of Four Alkylsilanes. NACA RM E51A05, 1951.

8. Pauling, Linus: The Nature of the Chemical Bond. Cornell Univ. Press, 2d ed., 1940.

9. Bichowsky, F. Russell, and Rossini, Frederick D.: The Thermochemistry of the Chemical Substances. Reinhold Pub. Corp. (New York), 1936.

10. Simon, Dorothy M., Wong, Edgar L., Levine, Oscar, and Gerstein, Melvin: Flame Propagation. The Effect of Molecular Structure on the Flame Velocities of Hydrocarbons. Abstracts of Papers 117th Meeting of Am. Chem. Soc., 1950, pp. 59(O)-60(O).

11. Sachsse, H., und Bartholomé, E.: Beiträge zur Frage der Flammengeschwindigkeit. Zeitschr. f. Elek., Bd. 53, Nr. 4, Aug. 1949, S. 183-190.

12. Rochow, Eugene G.: Chemistry of the Silicones. John Wiley and Sons, Inc., New York, 1946.

TABLE I - COMPARISON OF PROPERTIES OF ALKYLSILANES WITH CORRESPONDING HYDROCARBONS

Fuel		Boiling point (°C)	Freezing point (°C)	Specific gravity	Heat of combustion (kcal/mole)	Maximum flame velocity (cm/sec)			Volume percent fuel at maximum U_f
Name	Formula					U_o	U_o-U_g	U_f	
Silane	SiH_4	-112[a]	-184[a]	0.68(-168° C)[a]	326.5[b]	(c)	(c)	(c)	
Methane	CH_4	-16[d]	-182[d]	.42(-164° C)[a]	213[d]	84.5[e]	75.0[e]	33.8[e]	9.96[e]
Monoethylsilane	$CH_3CH_2SiH_3$	-14[f]	<-100[f]		630[b]	>560			
Propane	$CH_3CH_2CH_3$	-42[d]	-188[d]	.58(-44° C)[a]	531[d]	99.5[e]	86.5[e]	39.0[e]	4.54[e]
Diethylsilane	$CH_3CH_2SiH_2CH_2CH_3$	56[f]	<-100[f]	.68[f]	933[b]	309	247	111	3.12
Pentane	$CH_3CH_2CH_2CH_2CH_3$	36[d]	-130[d]	.63[d]	845[d]	98.0[e]	85.3[e]	38.5[e]	2.92[e]
Trimethylsilane	$(CH_3)_3\ SiH$	9[f]	<-100[f]		765[b]	252	203	92	3.74
2-Methylpropane	$(CH_3)_3\ CH$	-12[d]	-160[d]	.6[a]	686[d]	87.5[e]	77.3[e]	34.9[e]	3.48[e]
Tetramethylsilane	$(CH_3)_4\ Si$	27[f]	-100[f]	.65[f]	911[b]	161	134	60	3.00
2,2-Dimethylpropane	$(CH_3)_4\ C$	9.5[d]	-17[d]	.6[a]	840[d]	83.0[e]	73.9[e]	33.3[e]	2.85[e]

[a]Handbook of Physics and Chemistry, Chemical Rubber Co., 28th edition, 1944.
[b]Calculated from bond energies (reference 6) for reaction

$$(C_nH_{2n+1})_r\ Si\ H_{(4-r)(gas)} + \frac{3nr+4}{2}\ O_{2(gas)} \longrightarrow SiO_{2(fused)} + nr\ CO_{2(gas)} + (nr+2)\ H_2O_{(liquid)}.$$

[c]Spontaneously inflammable.
[d]Selected Values of Properties of Hydrocarbons, National Bureau of Standards, 1947. Heat of combustion for reaction

$$C_nH_{2n+2(gas)} + \frac{3n+1}{2}\ O_{2(gas)} \longrightarrow n\ CO_{2(gas)} + (n+1)\ H_2O_{(liquid)}.$$

[e]Reference 1.
[f]Reference 7.

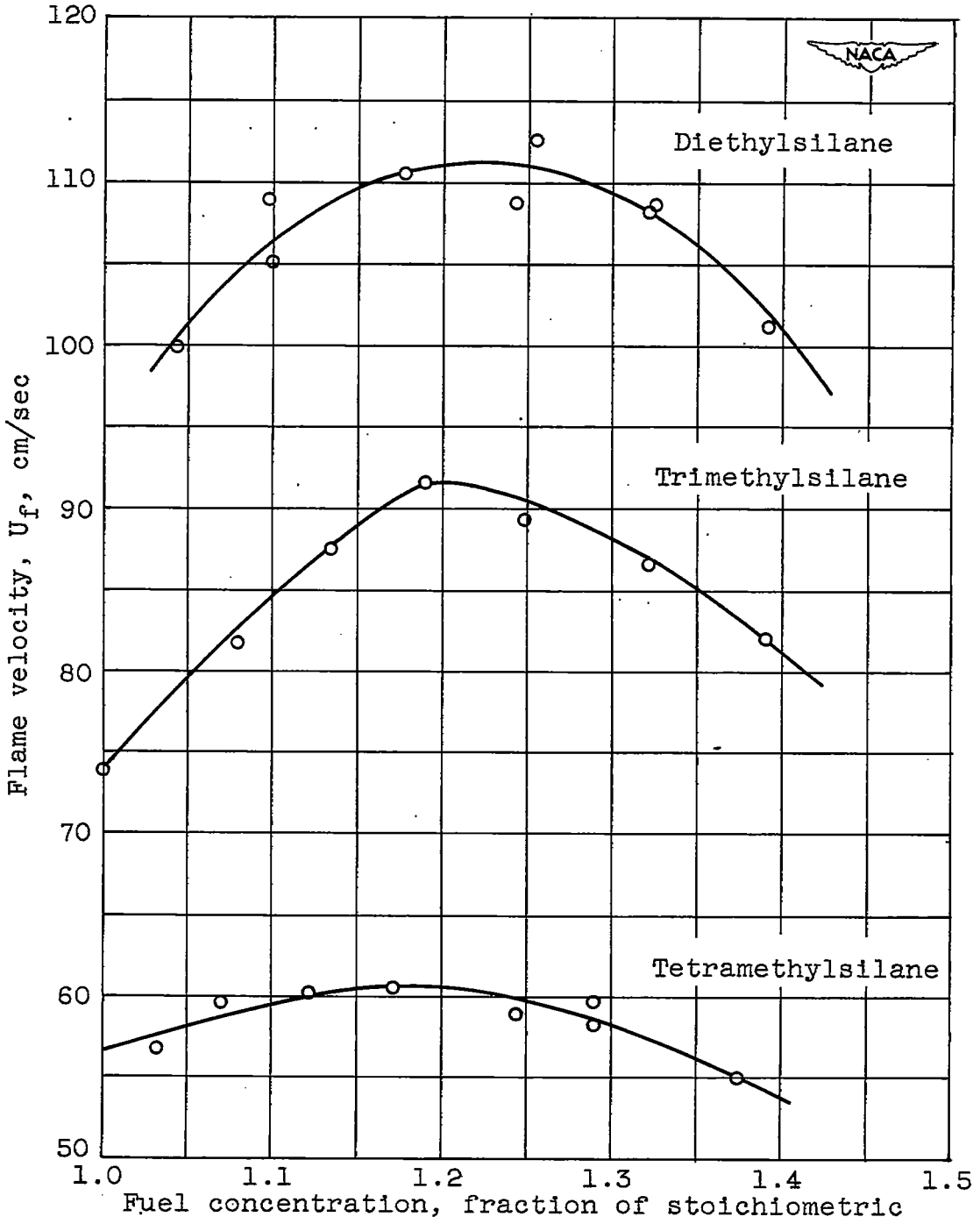

Figure 1. - Fundamental flame velocity of silanes.

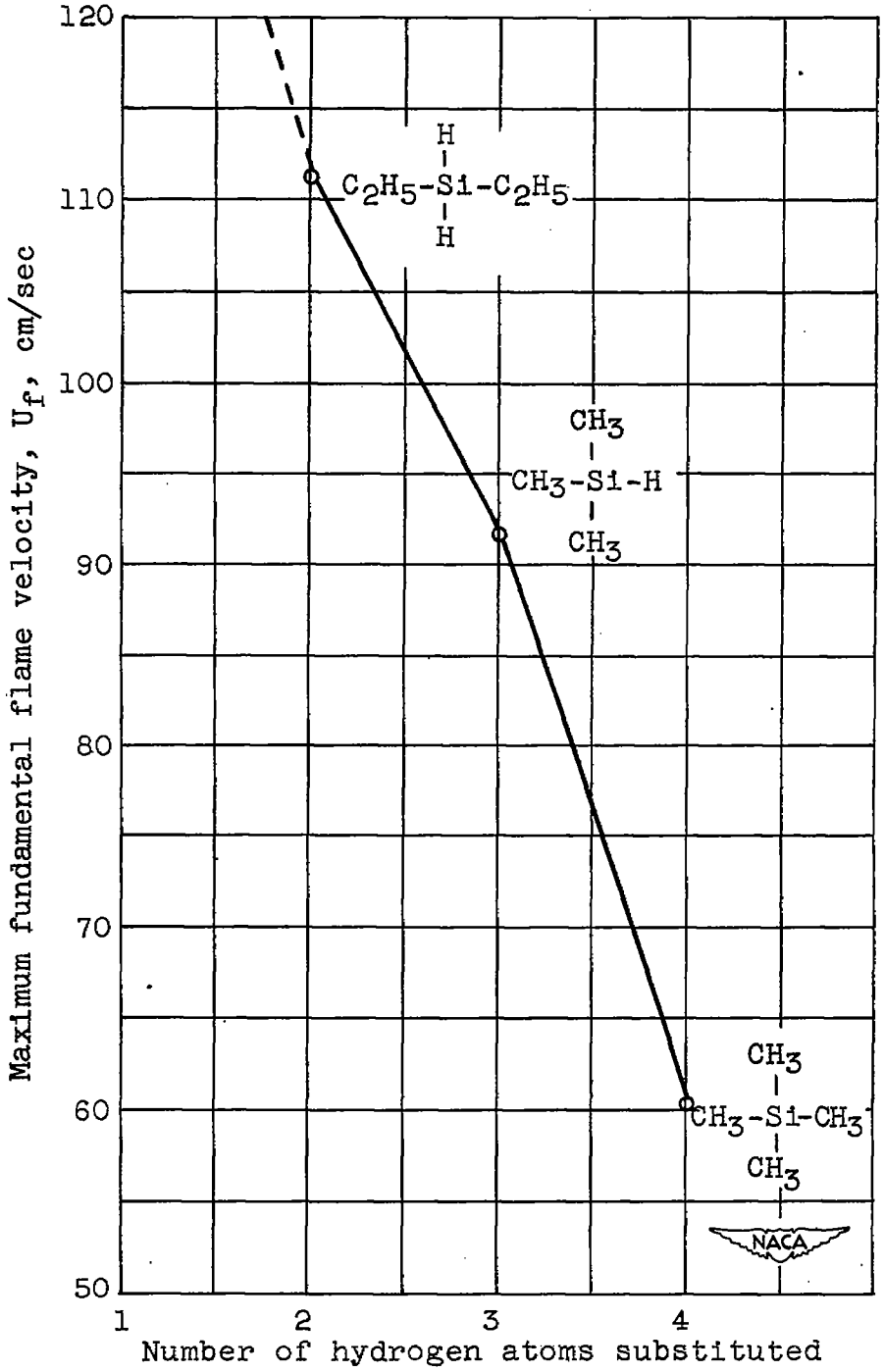

Figure 2. - Effects of substituting hydrogen atoms with alkyl groups.

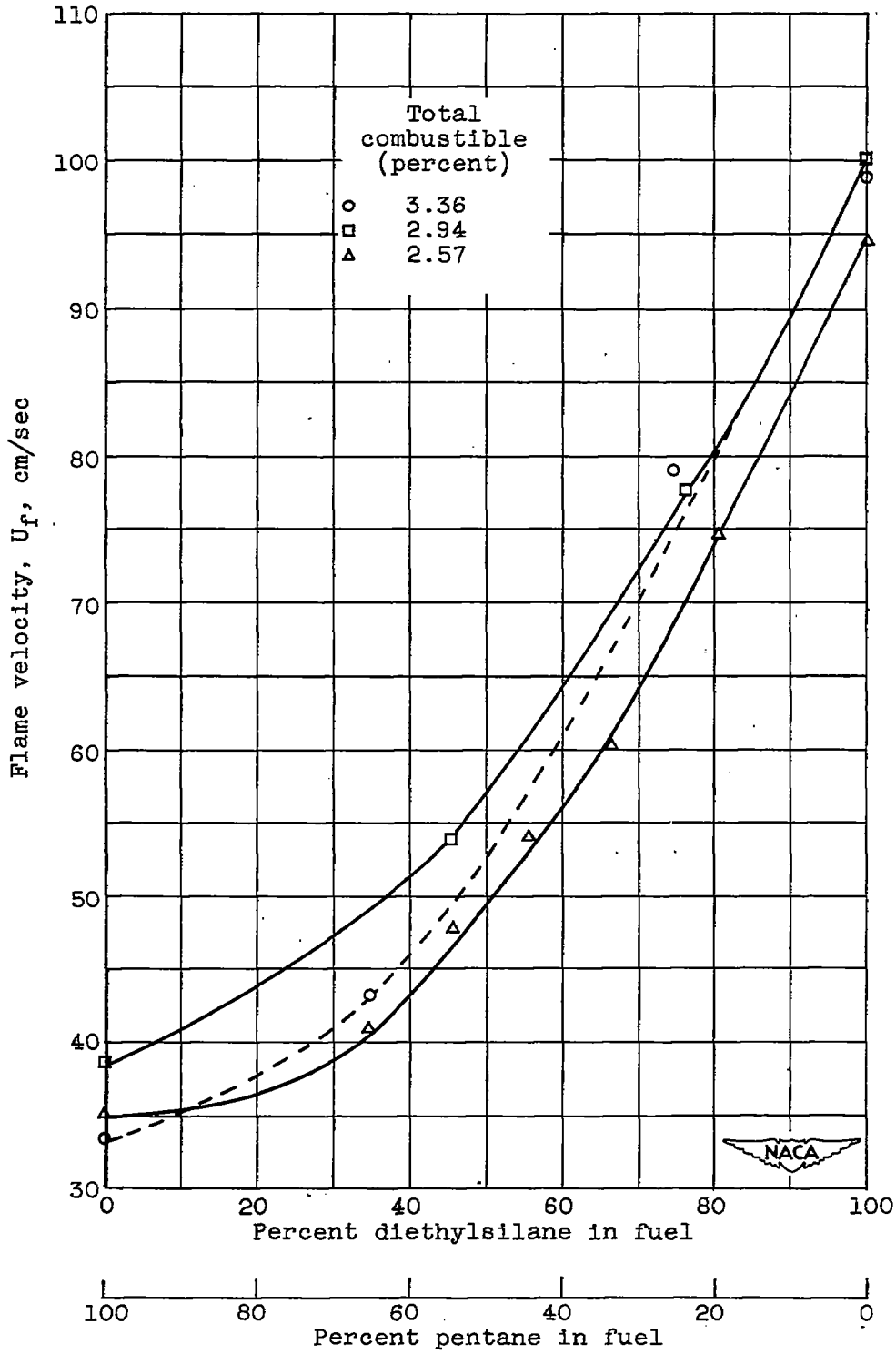

Figure 3. - Fundamental flame velocity of diethylsilane-pentane-air mixtures.

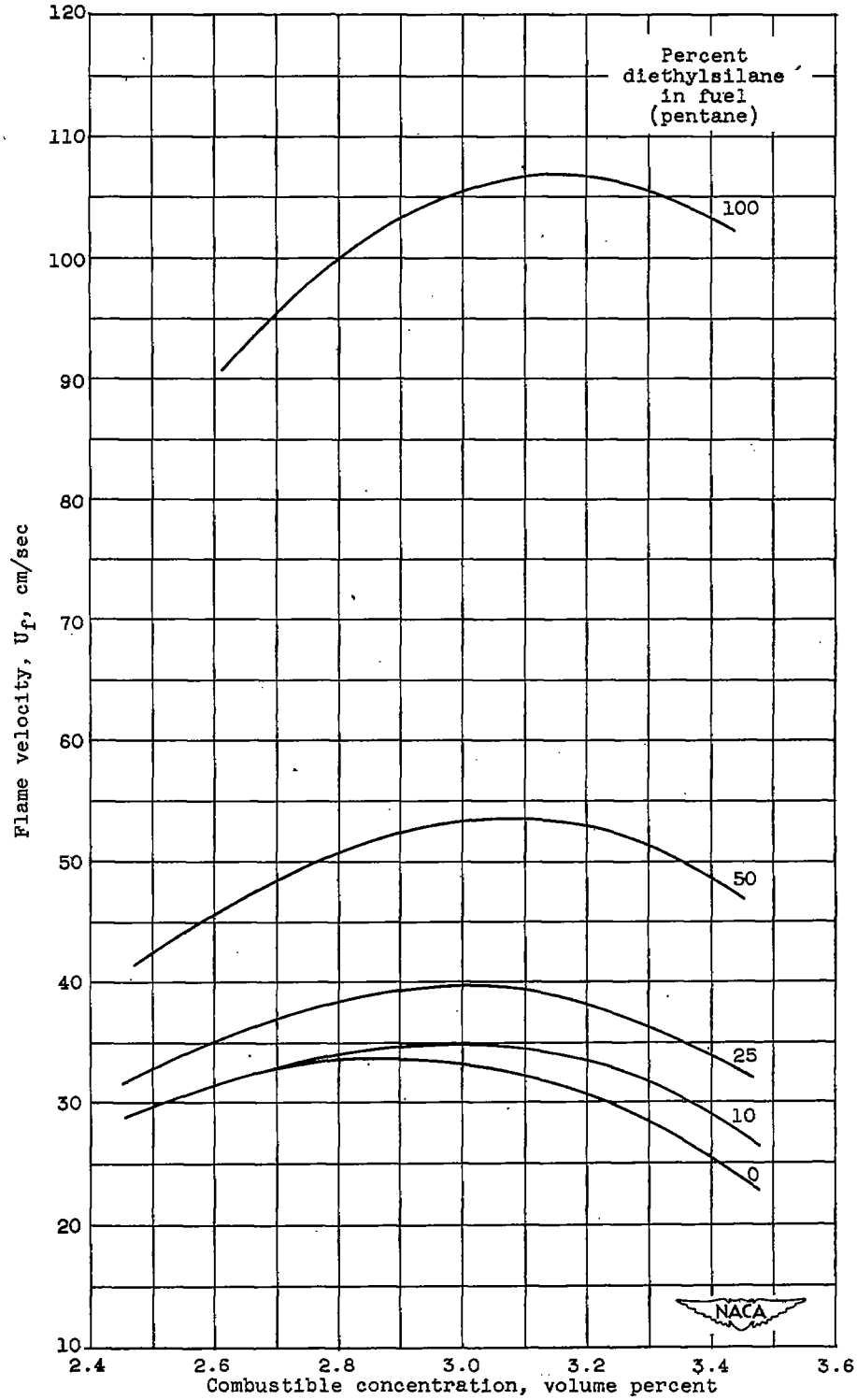

Figure 4. - Effect of concentration on flame velocity of diethylsilane-pentane-air mixtures.

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