

[CONTRIBUTION FROM THE DIVISION OF FUEL TECHNOLOGY AT THE PENNSYLVANIA STATE COLLEGE]

Hydrocarbon Burning Velocities Predicted by Thermal Versus Diffusional Mechanisms¹

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The maximum burning velocities for 36 hydrocarbon-air mixtures are predicted by the semi-empirical thermal equation of Semenov and compared with N.A.C.A. experimental velocities and those predicted by the semi-empirical Tanford and Pease diffusional equation, as previously calculated. Both correlations are based on the assumption that the specific reaction rate constant for the chemical reactions controlling the respective mechanisms are independent of hydrocarbon. Like the diffusional theory, the thermal correlation also shows that the combustion mechanism for the majority of the hydrocarbons is strikingly similar. For example, if a constant frequency factor is assumed in the Semenov equation, a variation of less than five per cent. in the activation energy brings the thermal result into line with experimental velocities for all mixtures except ethylene and acetylene.

Recently Simon² showed the maximum burning velocities for 35 hydrocarbons to be consistent with the active particle diffusion theory of flame propagation, as postulated by Tanford and Pease.³ However, as is recognized by Simon, the correlation is chiefly one involving the equilibrium flame temperature since the calculated radical concentrations depend primarily on this variable. It would, therefore, appear likely that a thermal mechanism which also depends primarily on the flame temperature might give a correlation with burning velocity equally as good as the active particle diffusion theory.

For the semi-empirical thermal correlation the general equation of Semenov,⁴ assuming a bimolecular reaction to be the controlling step, is used. The use of this thermal equation for evaluation of the burning velocities of a series of hydrocarbon compounds is tenable if the basic assumption is made that for all of the hydrocarbon-air mixtures considered, heat capacity, diffusivity, density and thermal conductivity and the variation of these properties with temperature can be described solely by the properties of air. Considering the fact that for all hydrocarbons studied the quantity of fuel in the mixture extends over the limited range from 2 to 10%, the thermal properties of the gaseous mixtures do not deviate appreciably from those of air. This is particularly true since the more a hydrocarbon's properties deviate from those of air, the lower, usually, is its percentage composition in the hydrocarbon-air mixture. Using the same temperature approximations as employed by Dugger,⁵ who simplified the Semenov equation for a propane-air mixture, the following general equation applicable to all hydrocarbons is obtained

$$\mu_t \propto \sqrt{\left[\left(\frac{n_1}{n_2}\right)^2 (K) \left(\frac{1}{E}\right)^3\right] \left[T_0^2 T_t^{4.9} e^{-E/RT_t} / (T_t - T_0)^3\right]} \quad (1)$$

where

n_1/n_2 = moles reactants/mole products by stoichiometric equation
 K = a frequency factor
 E = activation energy
 T_0 = initial mixture temperature
 T_t = calculated equilibrium flame temperature

The first three terms of equation (1) are essentially temperature independent and solely properties of the hydrocarbon-air mixtures. The term n_1/n_2 , of course, is easily calculated for each mixture and is taken into account. Unlike the simplified diffusional equation which has only one unknown, the specific reaction rate constant, the simplified thermal equation has two unknowns, the frequency factor and the activation energy for combustion initiation. If the thermal equation is to be used for predicting relative flame velocities, it is necessary to assume both unknowns independent of fuel-air mixture. In essence the hypothesis that the frequency factor and activation energy are constants in the thermal equation implies that the specific rate constant for the chemical reactions involved in the thermal mechanism are invariant for all hydrocarbons. That this may have some justification as an initial assumption is seen from the fact that Simon² found the specific reaction rate constant in the diffusional equation virtually independent of hydrocarbon. This was interpreted as an indication of a similar reaction mechanism for all hydrocarbons.

Since activation energy is also involved in the temperature dependent part of equation (1), it is necessary to select a reasonable activation energy for the correlation. Limited experimental data which have been found on activation energies for low temperature hydrocarbon oxidation (ethane,⁶ propane,⁶ pentane⁶ and ethylene⁷ yield values from 38 to 42 kcal./mole.⁸ If a value of 40 kcal./mole is then assumed for the heat of activation of all hydrocarbon-air mixtures and K is taken as a constant, the relative values of burning velocity may be expressed by the following form of equation (1)

$$\mu_t \propto \frac{n_1}{n_2} \sqrt{T_t^{4.9} e^{-40,000/RT_t} / (T_t - T_0)^3} \quad (2)$$

where n_1/n_2 and T_t pertain to the hydrocarbon in question. The relative values of burning velocity for 36 hydrocarbon-air mixtures at room temperature, 300°K., are then converted to absolute values by using the maximum experimental velocity of

(6) W. Jost, "Explosion and Combustion Processes in Gases," McGraw-Hill Book Co., Inc., New York, N. Y., 1946, pp. 427, 437 and 401.

(7) H. W. Thompson and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A125**, 277 (1929).

(8) Heats of activation were also found for methane and benzene, but these compounds are known to give anomalous oxidation results and higher heats of activation than the other members of the hydrocarbon series. Therefore, they were not considered in selecting a mean activation energy for the hydrocarbons.

(1) Presented before the Division of Gas and Fuel Chemistry of the American Chemical Society, New York, N. Y., September, 1951.

(2) D. M. Simon, *This Journal*, **73**, 424 (1951).

(3) C. Tanford and R. N. Pease, *J. Chem. Phys.*, **15**, 861 (1947).

(4) N. N. Semenov, *Progress of Phys. Sci. (U.S.S.R.)*, **24**, No. 4 (1940).

(5) G. L. Dugger, *This Journal*, **72**, 5271 (1950).

propane-air, 39.0 cm./sec., as the reference mixture, and the results are presented in Table I. A comparison of the burning velocities as predicted by the Tanford and Pease and by the Semenov equations with the experimental results show that for the straight chain alkanes the agreement is, for the most part, good. That the Semenov equation predicts too high a burning velocity for methane is expected since the heat of activation of methane-air mixtures is reputed to be considerably higher than 40 kcal./mole.⁹ For the branched-chain alkanes and alkenes both the thermal and diffusional equations predict burning velocities that are too high. The diffusional theory appears to predict high values because the specific reaction rate constant for branched-chain compounds is somewhat lower than the average value assumed for all hydrocarbon-air mixtures. The thermal equation predicts a still higher value, probably due both to deviations in the frequency factor and heat of activation from the average. An indication of a deviation in activation energy was expected since branched chain compounds do have higher ignition temperatures¹⁰ and, therefore, probably higher activation energies than their straight-chain counterparts. For normal alkenes the values predicted by the two equations are in relatively good agreement with experimental results except for ethylene. It is particularly interesting that both the thermal and diffusional equations predict very nearly the same velocity for ethylene. Certainly both mechanisms

TABLE I
BURNING VELOCITIES OF HYDROCARBON FLAMES

Compounds	Vol. % hydrocarbon ^a	T _{ig} , °K.	Flame velocity, cm./sec.		
			Exptl. ^a	Semenov equation	Tanford equation
Methane	9.96	2235	33.8	40.2	33.9
Ethane	6.28	2246	40.1	39.2	37.1
Propane	4.54	2251	39.0	39.0	37.7
Butane	3.52	2256	37.9	39.4	37.6
Pentane	2.92	2249	38.5	38.2	37.5
Hexane	2.51	2241	38.5	37.2	37.3
Heptane	2.26	2208	38.6	34.8	38.0
2-Methylpropane	3.48	2259	34.9	39.9	36.9
2,2-Dimethylpropane	2.85	2254	33.3	39.8	36.2
2-Methylbutane	2.89	2253	36.6	38.8	37.1
2,2-Dimethylbutane	2.43	2254	35.7	38.5	36.8
2,3-Dimethylbutane	2.45	2252	36.3	39.1	37.0
2,2,3-Trimethylbutane	2.15	2242	35.9	37.0	36.6
2-Methylpentane	2.46	2251	36.8	38.2	37.2
3-Methylpentane	2.48	2245	36.7	37.6	37.1
2,3-Dimethylpentane	2.22	2220	36.5	35.2	36.2
2,4-Dimethylpentane	2.17	2236	35.7	36.6	36.4
Ethylene	7.40	2387	68.3	54.7	52.9
Propene	5.04	2341	43.8	48.9	45.3
1-Butene	3.87	2320	43.2	45.7	42.8
1-Pentene	3.07	2316	42.6	44.4	42.8
1-Hexene	2.67	2237	42.1	42.0	41.7
2-Methylpropene	3.83	2315	37.5	45.2	42.0
2-Methyl-1-butene	3.12	2298	39.0	42.7	41.2
3-Methyl-1-butene	3.11	2305	41.5	43.6	42.2
2-Ethyl-1-butene	2.65	2284	39.3	41.7	40.7
2-Methyl-1-pentene	2.80	2237	39.6	36.8	39.2
4-Methyl-1-pentene	2.62	2295	40.5	42.7	41.3
Acetylene ^{a,b}	10.00	2611	131.0	86.5	88.6
Propyne	5.86	2472	69.9	64.9	61.3
1-Butyne	4.36	2413	58.1	55.7	55.6
1-Pentyne	3.51	2370	52.9	50.8	51.6
1-Hexyne	2.97	2333	48.5	46.0	48.6
2-Butyne	4.36	2401	51.5	54.6	53.3
Cyclohexane	2.65	2249	38.7	38.3	37.4
Benzene	3.34	2307	40.7	44.5	40.4

^a Experimental burning velocity taken from Jost, "Explosion and Combustion Processes in Gases," p. 122.
^b Equilibrium flame temperature calculated by authors.

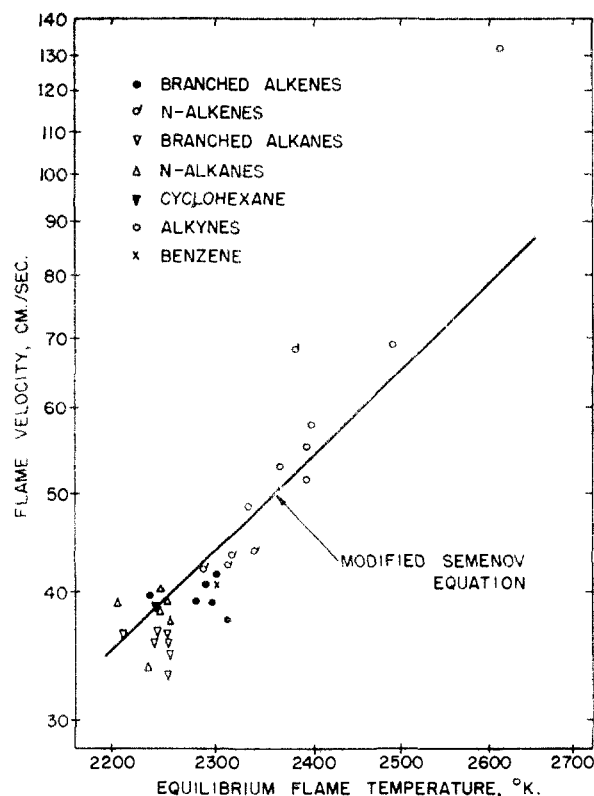


Fig. 1.—Correlation between burning velocity and equilibrium flame temperature.

(9) W. Jost, "Explosion and Combustion Processes in Gases," McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 422.

(10) J. L. Jackson, *Ind. Eng. Chem.*, **43**, 2869 (1951).

substantiate the belief that the ethylene-air combustion reactions are quite different from other hydrocarbons. The burning velocities predicted for the normal alkynes are in relatively good agreement with experiment except for acetylene, which deviates markedly. Its deviation is expected when predicted by the thermal equation since the heat of activation of acetylene has been shown to be considerably lower than 40 kcal./mole.¹¹ However, a deviation also in the reaction mechanism for acetylene is indicated by the considerable difference between the diffusional equation and experimental results.

In general, the diffusional equation predicts the burning velocity of the room temperature hydrocarbon mixtures more closely than does the thermal equation. Examination of the two equations does indicate, however, that the thermal equation is more sensitive to a given per cent. change in the reaction rate constant than is the diffusional equation.

(11) W. Jost, ref. 9, p. 403.

Therefore, the assumption of an invariant rate constant, if incorrect to any degree, would result in a thermal correlation that is not as satisfactory as a diffusional correlation. However, beyond this point it is impossible to state whether the difference in correlation is due to the fact that either the reaction rate constant in the thermal equation is more affected by hydrocarbon or that the thermal mechanism less closely predicts the true combustion phenomenon.

Simon² has plotted the variation in burning velocity solely as a function of flame temperature and has remarked on the good correlation obtained. It is interesting to note that equation (2) predicts directly the variation in burning velocity with flame temperature if the mole ratio, n_1/n_2 , is assumed independent of hydrocarbon-air mixture. This is a justifiable approximation since, near the stoichiometric mixture where maximum burning velocity occurs, the ratio rarely varies by more than two per cent. from the mean. Figure 1, then, is a log-log plot of burning velocity predicted by equation (2), using the experimental value of propane as a basis, versus the calculated equilibrium flame temperature with n_1/n_2 a constant. The equation plots essentially as a straight line predicting that the burning velocity varies approximately as the 4.9 power of the flame temperature. Disregarding the burning velocities of ethylene and acetylene, which give anomalous results with both theories, the rate of change of burning velocity with equilibrium flame

temperature is satisfactorily predicted by the modified Semenov equation. It is not certain whether the fact that the predicted rate of change is not quite as great as actually occurs is due to the choice of a slightly low average activation energy, to a progressive increase of the frequency factor with decreasing chain length of the alkynes or to an activation energy for the alkynes that is progressively lower than the assumed value. However, it would not seem to be due to the selection of a low average activation energy for two reasons. First, the trend of the alkynes with decreasing chain length appears to be toward lower activation energy and higher frequency factor, as is exemplified in acetylene. Second, since the activation energy value selected was from available data on low temperature hydrocarbon oxidation, it would be expected that the value would be too high rather than too low when applied to activation at combustion temperatures.

A variation of less than 5% in activation energy will bring the calculated burning velocities, as shown by the modified Semenov equation, in line with experimental values for all mixtures except ethylene and acetylene. This is an indication that the initial assumption of the constancy of the frequency factor and activation energy was justifiable. Furthermore, it again stresses the fact that both thermal and diffusional theories indicate a marked similarity of most hydrocarbons for the combustion reaction.

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Physical Properties of Perfluoro-*n*-hexane and Perfluoro-2-methylpentane

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Samples of two isomeric perfluorohexanes have been prepared by the fluorination of the pure hydrocarbons with cobalt trifluoride. The resulting crude products were fractionally distilled and the best cuts of each were combined. These were used for determinations of melting point, vapor pressure, surface tension, viscosity, density and index of refraction. Of the two compounds the normal fluorocarbon is the less dense, the less viscous and the more volatile. Its surface tension and index of refraction are the lower. The liquids are very much alike, but their physical properties differ from each other somewhat and in directions opposite to those for the corresponding hydrocarbons. In this respect they resemble perfluoro-*n*-pentane and perfluoroisopentane.

While it is well known that fluorocarbon isomers closely resemble each other in many ways, it is still the case that only a few specific examples may be cited as evidence for this generalization. The most thoroughly studied example is that of perfluoro-*n*-pentane vs. perfluoro-isopentane.¹⁻⁵

A number of properties of two isomers of perfluorohexane are reported in this paper.

Experimental

Preparation of Fluorocarbons.—These compounds were prepared by the fluorination of hydrocarbons with cobalt

trifluoride using the apparatus and procedures of Barber, Burger and Cady.¹

The hydrocarbons were of high quality, being Research Grade products of the Phillips Petroleum Company. Analyses reported by the Company were: *n*-hexane, 99.85 ± 0.05 mole %; 2-methylpentane, 99.74 ± 0.06 mole %. It is assumed that the predominant perfluorohexanes in the products were of the same structure. Following the fluorination of the hydrocarbons, the resulting crude fluorocarbons were refluxed with an alkaline solution of potassium permanganate, to remove unsaturated compounds, and were then carefully distilled using a fractionating column shown under test to have about 82 theoretical plates. During the distillations cuts of about 10-ml. volume were taken, and those from the middle region of each distillation temperature plateau were later combined. Such blended samples were used for the determination of physical properties other than the melting points.

From 217 g. of *n*-hexane about 585 g. of crude fluorocarbon boiling above 50° was obtained. The distillation yielded 245 g. of a "plateau" product having a head temperature range from 57.08 to 57.30°. Fractions having a distillation range from 57.11 to 57.12° were combined to make the sample used for studies of physical properties.

(1) E. J. Barber, L. L. Burger and G. H. Cady, *THIS JOURNAL*, **73**, 4241 (1951).

(2) L. L. Burger and G. H. Cady, *ibid.*, **73**, 4243 (1951).

(3) G. H. Rohrbach and G. H. Cady, *ibid.*, **71**, 1938 (1949).

(4) F. L. Mohler, E. G. Bloom, J. H. Lengel and C. E. Wise, *ibid.*, **71**, 337 (1949).

(5) D. C. Smith, *et al.*, Naval Research Laboratory Report 3567, "Spectroscopic Properties of Fluorocarbons and Fluorinated Hydrocarbons," 1949, pp. 128, 129.