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OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

A Comparison of the Burning Velocities of Methane and Heavy Methane in Nitrogen and Argon "Airs" at Atmospheric Pressure[1]

BY WILLIAM H. CLINGMAN AND ROBERT N. PEASE

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In order to determine whether diffusion or heat conduction is more important in flame propagation, the burning velocities of methane (CH_4) and heavy methane (CD_4) were measured at atmospheric pressure and in both nitrogen and argon "airs." The Semenov bimolecular equation, based on a thermal theory of flame propagation, predicted a much greater increase in the burning velocity than was observed on going from nitrogen–air to argon–air. The ratio of the burning velocity of a mixture with CH_4 to that of a mixture with CD_4 of the same composition was always greater than one and increased with increasing concentration of fuel. This behavior is in qualitative agreement with a diffusion mechanism. It is shown that a thermal theory does not account for this increase in the burning velocity ratio if it is assumed that changes in the thermal properties of the system such as thermal conductivity, flame temperature, and heat capacity can be neglected upon replacing CH_4 with CD_4.

One of the major unsolved problems in the field of combustion today is the mechanism of flame propagation. Simon[2] has recently reviewed the experimental investigations which have been conducted in order to distinguish between the thermal and diffusion mechanisms of flame propagation. In the former model it is assumed that the conduction of heat from the flame front into the unburned gas is rate controlling while in the diffusion model it is assumed that the rate-controlling steps are the diffusion of active species from the flame front into the unburned gas and subsequent reaction with the fuel. In order to elucidate the relative importance of these two mechanisms the authors[3,4] have measured the burning velocities at reduced pressure of methane–air mixtures in which the nitrogen in the air was substituted with argon or helium. These measured burning velocities were then compared with the Tanford–Pease[5] and Semenov[6] equations of burning velocity based on the diffusion and thermal mechanisms, respectively.

To test further the applicability of these two theories it was proposed that the burning velocities of CH_4 and CD_4 be compared at one atmosphere and varying compositions. Upon replacing the hydrogen atoms in the CH_4 with deuterium atoms only small changes are made in the flame temperature and thermal conductivity of the mixture. The equilibrium atom and radical concentrations are lower in the case of the heavy methane, however, the lower zero point energy of the deuterated compounds compared with the protonated compounds resulting in somewhat decreased dissociation at the flame front into atoms and radicals. The diffusion coefficients for deuterium atoms are also lower than those for hydrogen atoms due to the greater mass of the former. Thus, on the basis of the diffusion mechanism one would expect a decrease in burning velocity on going from CH_4 to CD_4; this decrease would be greater the higher the concentration of deuterium atoms compared to the concentration of the other active species. The burning velocities calculated by a thermal theory, however, will be less dependent on the relative concentration of deuterium atoms at the flame front.

In order to study the effect of isotopic substitution at two appreciably different flame temperatures, measurements of the burning velocity were made over a range of compositions using both nitrogen–air and argon–air.

Experimental

Preparation of CD_4.—The CD_4 was prepared by the decomposition of Al_4C_3 with D_2O following the procedure of Taylor and Wright.[7] The Al_4C_3 and liquid D_2O were refluxed, the temperature of the reactants being equal to the boiling point of the heavy water at the pressure in the system. Carbon dioxide was added to the reaction system in order to keep the pressure at all times above one-half atmosphere and, thus, the temperature of the reactants above about 80°.

The Al_4C_3 was obtained from the Baird Company and was dehydrated by heating *in vacuo* with a flame. The D_2O was obtained from the Stuart Oxygen Company, who listed the isotopic purity as 99.5%. The heavy water was degassed and distilled before use. The CO_2 was obtained from Dry Ice, small amounts of air and water being removed by freezing down in liquid nitrogen, pumping, and subliming about $^5/_6$ of the solid CO_2. This procedure was repeated three times.

The crude product from the decomposition of the Al_4C_3 contained CD_4, CO_2, about 7% D_2,[7] and smaller amounts of higher deuterocarbons. The D_2 was first removed by freezing out the other components of this mixture in a trap surrounded by liquid nitrogen under a pressure of 2–3 cm. (temperature = 57°K.). The bulk of the CO_2 was removed

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[1] Taken from a thesis submitted by William H. Clingman in partial fulfillment of the requirements for the Ph.D. degree. The work described in this paper was carried out at Princeton University in connection with Contract NOrd 7920 with the United States Naval Bureau of Ordnance, as coördinated by the Applied Physics Laboratory, The Johns Hopkins University, and Contract N6ori 105 with the Office of Naval Research and Office of Scientific Research (Air Force) and the Office of Ordnance Research (Army) as coördinated by Project Squid, Princeton University. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] D. M. Simon, "Diffusion Processes as Rate-Controlling Steps in Laminar Flame Propagation," Colloquium held by the Advisory Group for Aeronautical Research and Development, North Atlantic Treaty Organization, at Cambridge, England, December 7–11, 1953.

[3] W. H. Clingman and R. N. Pease, to be published.

[4] W. H. Clingman, R. S. Brokaw and R. N. Pease, "Fourth Symposium on Combustion," The Williams and Wilkins Co., Baltimore, Md., 1953, pp. 310–313.

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

[6] N. N. Semenov, *Prog. Phys. Sci.* (*USSR*), **24**, No. 4 (1940). Translation appears as N.A.C.A. TM No. 1026, 1942.

[7] M. M. Wright and H. S. Taylor, *Can. J. Research*, **27B**, 303 (1949).

by passing the gaseous product through a trap surrounded by a mixture of solid and liquid methylcyclopentane (133°K.) or alternatively by distillation from a trap at 74°K. (liquid nitrogen) to one at 57°K. Two final distillations from 74 to 57°K. removed the remainder of the impurities. The heavy methane prepared in this manner was of high purity.[8]

Determination of Burning Velocity.—The apparatus for measuring the flame velocity of the CD_4 was essentially that used by Brokaw[9] in determining the effect of water vapor on the burning velocities of cyanogen–oxygen–argon mixtures. A brass, water cooled burner, 0.896 cm. in diameter, was used, the initial temperature of the combustible mixtures being kept at 25° for all runs. The burner was surrounded by a glass mantle, 64 mm. in diameter and provided with two 4 inch diameter tempered glass windows, through which the flame was photographed. The photographs were made with a 4 × 5 Speed Graphic camera at $^1/_{10}$ sec. and a lens opening of F 4.7 on Kodak Plus-X film. In order to determine the burning velocity the modified angle method previously described[3] was used.

As a check on the experimental procedure the flame velocity of C.P. CH_4 supplied by the Matheson Company was determined at four different compositions in N_2–air using the above "CD_4" apparatus. Measurements were also made with this apparatus of the burning velocity of CH_4, N_2–air mixtures, the CH_4 having been prepared from Al_4C_3 and H_2O. It can be seen in Fig. 1 that the results are in agreement with those obtained previously.[3]

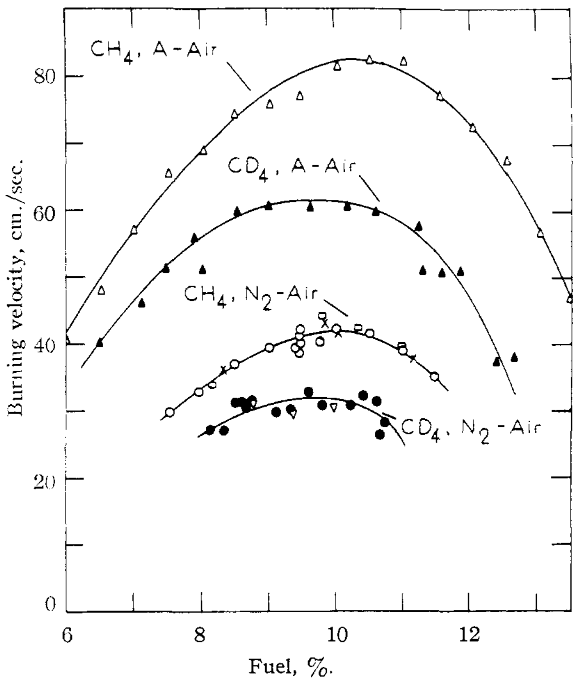

Fig. 1.—Burning velocities of methane and heavy methane in nitrogen and argon "airs": □, C.P. CH_4 with "CD_4" apparatus; ∇, CD_4 (made for A-air runs) with N_2-air; ×, CH_4 (made from Al_4C_3 + H_2O) with N_2-air; stoichiometric mixture is 9.5% CH_4.

Two batches of CD_4 with identical infrared spectra were used, one for the runs with N_2-air and one for those with argon-air. It can be seen from Fig. 1 that burning velocities in N_2–air of samples from both batches were in agreement.

The argon and oxygen were obtained from the Matheson and American Oxygen Company, respectively, while the air was obtained from the laboratory supply and dried over $CaCl_2$.

Discussion of the Results

The experimental burning velocities for CD_4 are given in Fig. 1 along with those obtained previously[3] for CH_4 in N_2–air and A–air. The flames with the CD_4, N_2–air mixtures were less stable than the corresponding ones with CH_4. In some cases the flame blew off before two photographs could be taken. Whenever possible, however, the results from two photographs were averaged in the burning velocity determination.

For the stoichiometric mixture there is about a 25% decrease in flame velocity when CD_4 is substituted for CH_4. With both the argon–air and the nitrogen–air the disparity increases as the mole fraction of fuel in the initial mixture increases. This behavior is predicted at least qualitatively by the diffusion theory. Friedman and Burke[10] in a similar study with C_2H_2 and C_2D_2 found that the burning velocity of the deuterated fuel was about 20% lower than that of the protonated compound.

Our experimental results have been compared with the predictions of both the Tanford–Pease and Semenov bimolecular equations for burning velocity. The former may be written[4]

$$S_0 = \left[\frac{0.7LT_0}{T_m} \sum_i (k_iP_iD_i)\right]^{1/2} \qquad (1)$$

where

S_0 = burning velocity
P_i = partial pressure of the ith active species at the flame front
D_i = the diffusion coefficient into the unburned gas for the ith active species
T_0 = the initial temperature
L = the number of molecules per cc. at T_0
T_m = a mean effective temperature for the combustion zone (taken as $0.7T_f$)
k_i = rate constant for the reaction of the ith active species with the fuel

The Semenov equation assuming a bimolecular reaction may be written[11]

$$S_0 = \left[\frac{2\lambda f \int_0^{T_f} w \, dT}{a_0\rho_0C_p} \left(\frac{n_1}{n_2}\right)^m \left(\frac{\lambda}{DC_p\rho}\right)_f^m\right]^{1/2} \qquad (2)$$

where

a = concentration of fuel
ρ = density
C_p = mean specific heat over the combustion wave
n_1/n_2 = moles of reactants per moles of products from stoichiometric eq.
w = reaction rate
D = diffusion coefficient
m = molecularity of flame reaction

The subscript 0 refers to the initial mixture, while the subscript f refers to the value at the flame temperature.

In calculating burning velocities by equation 2 the integral, $\int_0^{T_f} w \, dT$, was evaluated by the same procedure as used by Dugger and Simon.[11] The quantity $(C_p + 5/4\ R/1.336C_p)_f^2$ was substituted for $(\lambda/DC_p\rho)_f^m$ in equation 2 using relationships also summarized by Dugger and Simon.

The system parameters such as thermal conductivity, diffusion coefficients, heat capacity, flame temperature, equilibrium atom and radical concentrations, and chemical constants were obtained in the same manner as previously.[3,4] It was as-

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[8] The authors wish to thank C. C. Schubert, S.J., for examining the infrared spectrum.

[9] R. S. Brokaw and R. N. Pease, This Journal, **75**, 1454 (1953).

[10] R. Friedman and E. Burke, *Ind. Eng. Chem.*, **43**, 2772 (1951).

[11] G. L. Dugger and D. M. Simon, "Fourth Symposium on Combustion," The Williams and Wilkins Company, Baltimore, Md., 1953, pp. 336–345.

TABLE I

FLAME TEMPERATURES AND EQUILIBRIUM ATOM AND RADICAL CONCENTRATIONS FOR MIXTURES OF CH_4 AND CD_4 WITH ARGON–AIR AND NITROGEN AIR AT ATMOSPHERIC PRESSURE

	CH_4				CD_4			
% Fuel	Flame temp., °K.	Radical concn. atm. × 10^4 H	OH	O	Flame temp. °K.	Radical concn. atm. × 10^4 D	OD	O
			Mixtures with nitrogen-air					
8	2036	0.381	19.1	1.67	2020	0.277	17.3	1.48
9	2175	1.99	29.0	2.61	2160	1.510	26.5	2.35
10	2218	5.58	19.1	0.979	2198	4.49	16.5	0.728
11	2142	6.14	6.28	0.125	2121	4.89	5.08	0.0884
			Mixtures with argon-air					
7	2274	2.71	55.8	10.7	2257	2.08	51.5	9.65
8	2408	9.02	85.1	18.2	2393	7.30	79.7	16.7
9	2494	20.1	101.4	21.0	2479	16.6	94.7	19.1
10	2531	32.9	94.5	16.7	2516	28.0	87.5	14.6
11	2517	41.7	67.6	8.21	2495	34.8	59.5	6.65
12	2441	38.8	34.0	2.27	2400	29.6	25.7	1.42

sumed that there was no change in the thermal conductivity of the mixtures upon replacing CH_4 with CD_4, and a value of 9.77 cal. deg.$^{-1}$ mole^{-1} was calculated for the heat capacity of CD_4 using the method given by Mayer and Mayer.[12] The equations given by Brokaw[9] were used to compute the equilibrium constants for the deuterated compounds, and enthalpies of the latter were determined from spectral data. The enthalpy of formation of OD was taken as +9.502 kcal. and that of CD_4 calculated to be −21.315 kcal./mole at 298°K. using the method suggested by Friedman.[10] The heats of formation of the other species were taken from Bureau of Standards Tables.[13] The values given by Simanoti[14] were used for the fundamental frequencies of CD_4, while the spectral data for the other deuterated compounds were taken from the 6th edition of Landolt–Börnstein.[15]

The activation energies of the reactions of the deuterated compounds were taken to be the same as those for the corresponding reactions of the protonated compounds, since the theoretical work of Bigeleisen[16] has indicated that the activation energy difference for isotopic reactions approaches zero at high temperatures.

In Table I are given the calculated flame temperatures and equilibrium atom and radical concentrations for corresponding mixtures of CD_4 and CH_4 in nitrogen and argon "airs." The diffusion coefficient of D was estimated to be about 27 to 28% lower than that of H, while only small changes were calculated for the diffusion coefficients of the other active species upon substituting CD_4 for CH_4.

The experimental burning velocities for CD_4 have been compared with relative theoretical values given by the Semenov and Tanford–Pease equations in Table II. For each of these equations the calculated values were multiplied by a constant so as to make the burning velocity calculated for the 9% mixture of CD_4 with N_2–air equal to 31.0 cm./sec., the experimental value. In making the calculations with the Semenov equation it was assumed that the flame temperature, heat capacity, and thermal conductivity of each CD_4 mixture were the same as those of the corresponding CH_4 mixture.

TABLE II

COMPARISON OF THEORETICAL AND EXPERIMENTAL BURNING VELOCITIES FOR MIXTURES OF CD_4 WITH NITROGEN-AIR AND ARGON-AIR AT ATMOSPHERIC PRESSURE

% CD_4	Burning velocity, cm./sec. Exptl.	Tanford-Pease	Semenov	Burning velocity ratio[a] (CH_4/CD_4)
		Mixtures with nitrogen-air		
8	26.2	22.8	25.4	1.27
9	31.0	(31.0)	(31.0)	1.27
10	31.8	25.6	34.8	1.32
11	26.2	15.7	34.4	1.49
		Mixtures with argon-air		
7	46.5	46.8	66.0	1.21
8	56.0	63.6	79.5	1.23
9	60.9	73.6	81.9	1.28
10	61.4	73.8	84.1	1.34
11	58.3	63.0	98.1	1.39
12	47.2	44.1	92.0	1.55

[a] Ratio of the observed burning velocity of CH_4 to that of CD_4 for mixtures of the same composition. Values in parentheses are assumed.

From Table II it can be seen that the Semenov equation gives values too high with the argon–air mixtures, the Tanford–Pease theory being in better agreement with the experimental values. In view of the uncertainties in the values used for the parameters (thermal conductivity, activation energies, etc.) of the system, it is difficult to judge, however, how much of the discrepancy exhibited in Table II between theory and experiment is due to the approximations used in the derivation of the theoretical equations.

If it is assumed that the thermal properties of the mixtures do not change upon substituting CD_4 for CH_4, then the Semenov equation predicts that the ratio of the burning velocity of a mixture with CH_4 to that of the corresponding mixture with CD_4 is a function of the flame temperature only. An increase in this burning velocity ratio was observed experimentally on going from lean to rich mixtures

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(12) J. E. Mayer and M. G. Mayer, "Statistical Mechanics," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 440–454.

(13) "Selected Values of Chemical Thermodynamic Properties." Circular of the National Bureau of Standards 500, U. S. Government Printing Office (1952).

(14) T. Simanoti, *J. Chem. Phys.*, **17**, 245 (1949).

(15) "Landolt-Börnstein," 6th edition, Springer Verlag, Berlin–Göttingen–Heidelberg, 1950.

(16) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

with both nitrogen–air and argon–air. As can be seen from Table I, however, there are compositions on the rich and lean sides corresponding to the same flame temperature. For such mixtures with the same flame temperature a thermal theory would predict the same values for the burning velocity ratio. It is true that the reaction rates for CH_4 and CD_4 mixtures will be somewhat different even though the activation energies are comparable. Thus, in using the Semenov equation to predict the burning velocity ratio the quantity $\left(\int_0^{T_f} w_{CH_4}\,dT/\int_0^{T_f} w_{CD_4}\,dT\right)^{1/2}$ will have a temperature independent factor different from unity. Although at a particular composition this factor may account for the observed burning velocity ratio, the Semenov equation still predicts that this ratio is the same for mixtures with the same flame temperature. Thus, a purely thermal theory does not account for the observed increase in the burning velocity ratio as the initial concentration of fuel increases.

The burning velocity ratios predicted by the Tanford–Pease theory are dependent on the values taken for activation energies and diffusion coefficients. There is also an uncertainty in the effect of isotopic substitution upon the rates of the reactions of the fuel with active species.[10] Thus, it would be difficult to form valid conclusions from a comparison of the experimental burning velocity ratios with those predicted by the Tanford–Pease equation. Nevertheless, it is significant that the ratios of flame speeds for light to heavy methane increase progressively in going from lean to rich mixtures, for this is the direction in which hydrogen and deuterium atom concentrations become more important relative to hydroxyl or oxygen.

In conclusion it is believed that the above analysis of the experimental burning velocities of CH_4 and CD_4 presents evidence in favor of a diffusion mechanism. The Tanford–Pease equation is in much better agreement with the experimental values for the mixtures with argon–air than the Semenov bimolecular equation. In addition it has been pointed out that it is unlikely that a thermal theory can explain the observed effect of composition on the ratio of the burning velocities of corresponding CH_4 and CD_4 mixtures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CONNECTICUT]

A Method for Analyzing Pressure–Time Curves of Gas Phase Reactions

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Two methods are given for deriving from an assumed reaction paradigm expressions for the time derivatives of the total pressure in terms of rate constants and stoichiometric constants or functions. Experimentally determined initial values for these derivatives can be obtained and their behavior compared with the behavior of these derived expressions.

The rate at which a substance undergoes a chemical reaction in the gas phase is frequently obtained by measuring the total pressure in the system as a function of time. Conventional treatment of such data is limited to an evaluation of the initial pressure, the initial rate of pressure increase and the time required for a given percentage increase in the total pressure. No method has been available for obtaining useful information from the shape of the pressure–time curve. The purpose of this paper is the presentation of such a method.

Evaluation of the Time Derivatives of the Pressure.—Since a numerical value for at least the first and second time derivatives of the pressure is required, it is necessary to obtain an analytical rather than a graphical representation of the data. This can be accomplished by using the data to obtain an equation of the form

$$P_T = a_0 + a_1t + a_2t^2 + a_3t^3 + \dots \qquad (1)$$

Fortunately, the ingenious abbreviated least-squares treatment of Baily[1] and Cox and Matuschak[2] is ideally suited to this purpose. Because of the nature of the experiment, it is easy to meet the sole requirement of this abbreviated method, *i.e.*, that the values of the independent variable (time) form an arithmetic progression. Using this procedure, evaluation of the four coefficients in a cubic equation can be accomplished in about 15 minutes with an automatic calculator.

From eq. 1, it follows that

$$a_0 = P_0 \qquad (2)$$

$$a_1 = (dP_T/dt)_{t=0} \qquad (3)$$

$$2a_2 = (d^2P_T/dt^2)_{t=0} \qquad (4)$$

$$6a_3 = (d^3P_T/dt^3)_{t=0} \qquad (5)$$

where P_0 is the initial pressure and P_T is the total pressure at time, t. Higher derivatives can, of course, be evaluated; however, the possibility of obtaining directly interpretable quantitative information from anything higher than the second derivative is remote except in the case of very simple reactions. In such cases the information so obtained is of the same nature as that obtained from the second derivative but is inherently less accurate. However, though lacking in accuracy, the numerical value of the third derivative can frequently be used to obtain information whose magnitude or sign may be of assistance in understanding more complex reactions. Regardless of whether the treatment is limited to an evaluation of the first and second derivatives or extended to include an evaluation of the third, it has been found that precision is greatly improved if the data are taken over a time range sufficiently large to require one

(1) J. L. Baily, *Ann. Math. Statistics*, **2**, 355 (1931).

(2) C. J. Cox and M. C. Matuschak, *J. Phys. Chem.*, **45**, 362 (1941).