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Critical Considerations in the Measurement of Burning Velocities of Bunsen Burner Flames and Interpretation of the Pressure Effect. Measurements and Calculations for Methane[1]

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RECEIVED NOVEMBER 17, 1955

In order to elucidate such questions as the mechanism of propagation and general nature of the chemical reactions for hydrocarbon flames, an investigation has been conducted of the burning velocity of methane under various conditions. The experimental results have been compared with the Semenov and a modified form of the Tanford–Pease theory of flame propagation. An improved Bunsen burner method of determining the burning velocity has been presented in which it is determined for each flame observed whether there is a region of the flame cone over which the flame velocity is constant. Values for the burning velocity are assigned to the mixture only in those cases where such a constant region is found. The method has been shown to give burning velocity values which are independent of flow rate and burner diameter. The burning velocity of stoichiometric mixtures of methane in nitrogen–air at sub-atmospheric pressures has been found to vary as the -0.25 power of the pressure near one atmosphere and as the -0.5 power near one-half atmosphere. The pressure exponent of stoichiometric methane, helium–air mixtures was found to be -0.2. These results could not be accounted for with the Semenov equation for a bimolecular reaction, which predicts a decrease in burning velocity rather than an increase with decreasing pressure. If a thermal theory is to explain the results, it is necessary to postulate the existence of an important first-order reaction in the combustion zone. On the other hand, the Tanford–Pease theory does predict the observed effect qualitatively, though not quantitatively. Burning velocities of methane in nitrogen, argon and helium "airs" were redetermined by the improved method with some modification of earlier results.

Tanford and Pease[2] have put forward a theory of burning velocity in which it is assumed that the rate-controlling step in a one-dimensional, laminar flame is the diffusion of active species from the flame front into the unburned gas and subsequent reaction of these species with the fuel. Semenov,[3] on the other hand, has considered both diffusion of the reactants and conduction of heat from the flame front into the unburned gas as important processes in flame propagation. To test the applicability of these theories the burning velocities of methane–air mixtures, in which the nitrogen in the air was substituted with argon and helium, were measured.[4]

In particular, we felt that further information about the kinetics of flame processes could be obtained by determining the effect of pressure on the burning velocities of methane–air mixtures. If it is assumed that the flame temperature is roughly independent of pressure, the Tanford–Pease theory predicts that the burning velocity should be approximately proportional to the inverse fourth root of the pressure, while the Semenov equation indicates that flame speed is independent of pressure for a bimolecular reaction.

A necessary prerequisite for such an investigation is a suitable method for the determination of burning velocity, since the errors involved in burning velocity measurements using a Bunsen burner flame are particularly important at reduced pressures. Thus, a comparison was made between several techniques for making such measurements, and a modified angle method is presented in which, we feel, these errors have been largely eliminated.

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

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

(4) W. H. Clingman, R. S. Brokaw and R. N. Pease, "Fourth Symposium on Combustion," The Williams and Wilkins Company, Baltimore, Md., 1953, p. 310.

Experimental

The apparatus used was the same as that described previously[4] except for the changes given below, which were made necessary by operation at reduced pressure. Water-jacketed copper burners were used with inside diameters of 0.896, 1.256, 1.603 and 2.059 cm., the water being kept at 25° in all cases. The diameter of the mantle was enlarged to 4 inches for the low pressure measurements, and tempered glass windows were used. The gases were metered at one atmosphere and then passed through a capillary tube to obtain the necessary reduction in pressure, the gas being pulled through the system by a size VSD 778 Kinney High Vacuum Pump. The pressure was kept constant to within $^1/_2$ mm. of Hg by an automatically controlled leak into the line leading to the pump, and a ballast tank was inserted between the pump and burner.

The flames were photographed directly and also by the direct shadow method as described previously.[4] Shadowgraphs were taken at only one camera position, however, and since the burning velocity obtained in this manner is a function of the film-to-burner distance, a correction was applied to the results. The magnitude of this correction was only 1 to 3% of the burning velocity, and was obtained by preliminary experiments. The frustum, total area and a modified angle method were used to compute the burning velocity and are discussed below. Enlarged tracings of the photographs were used for the frustum and total area calculations, while the measurements involved in the angle method were made on an 8″ × 10″ photographic enlargement. The photographs were taken with a 4″ × 5″ Speed Graphic camera on Kodak Plus-X film. The exposure time ranged from $^1/_{10}$ to $^1/_{50}$ sec., and for most photographs of the visible cone the film was pre-exposed to a white background, cutting the required exposure time in half.

Air was obtained from the laboratory supply and dried over calcium chloride. For some of the runs air dried in this manner was passed over magnesium perchlorate with no noticeable effect on the burning velocities. It was thus concluded that the calcium chloride was sufficient to remove any water vapor that might influence the results. Helium and oxygen were obtained from the American Oxygen Company, while the Matheson Company supplied the argon and C.P. methane.

Calculation of Burning Velocity.—In a Bunsen burner cone with cylindrical symmetry the apparent burning velocity in general decreases from the tip of the flame to the base. As discussed by Lewis and von Elbe,[5] near the tip the cylindrical curvature causes the burning velocity to be greater than its value for a plane wave front, due to the convergence of heat flow and diffusional flow of radicals into the unburned gas. On the other hand the burner lip itself has a quenching effect on the flame, thus causing the burning velocity near the base of the flame to be lower than the true value for the mixture. There will therefore be a region midway along the flame cone where the burning velocity has its true value. The latter may be evaluated as follows. Let

r = radius of the flame cone at a given point
R = radius of the burner
$S(r)$ = local burning velocity as a function of r in cm./sec.
S_0 = true burning velocity

If there exists a range of values of r between $r = 0$ and $r = R$ such that $S(r) = S_0 =$ a constant, then S_0 so calculated should represent the true burning velocity. If, on the other hand, the errors due to curvature or to quenching tend to overlap, $S(r)$ would decrease continuously and no reliable value of S_0 would be obtained.

The following modification of the angle method was applied, laminar flow being assumed. Let

$U(r)$ = linear flow rate as a function of r in cm./sec.

$$U(r) = \frac{2V}{\pi R^4}(R^2 - r^2) \qquad (1)$$

The burning velocity may be defined as the component of the linear flow rate perpendicular to the flame cone at a given point

$$S(r) = U(r) \sin \alpha(r) \qquad (2)$$

where

$\alpha(r)$ = angle between the burner axis and the tangent to the flame cone at the point under consideration

Let

l = distance from the tip of the flame *measured along the inner boundary* of the flame cone

$$\frac{\mathrm{d}r}{\mathrm{d}l} = \sin \alpha(r) \qquad (3)$$

$$S(r) = \frac{2V}{\pi R^4}(R^2 - r^2)\frac{\mathrm{d}r}{\mathrm{d}l} \qquad (4)$$

Let

$$Z = \frac{r}{R} - {}^1/_3\left(\frac{r}{R}\right)^3, \text{ then}$$

$$\frac{\mathrm{d}Z}{\mathrm{d}l} = \left[\frac{1}{R} - \frac{1}{R}\left(\frac{r}{R}\right)^2\right]\frac{\mathrm{d}r}{\mathrm{d}l} = \frac{1}{R^3}[R^2 - r^2]\frac{\mathrm{d}r}{\mathrm{d}l}$$

Therefore

$$S(r) = \frac{2V}{\pi R}\frac{\mathrm{d}Z}{\mathrm{d}l} \qquad (5)$$

From (5) it is obvious that if there is a range of values for l over which the burning velocity is a constant, then a plot of Z against l will be a straight line with a slope equal to $\pi R S_0/2V$.

For each flame a plot of Z against l was made, and if this plot had a linear section which extended over at least one-third of the cone, the slope of this linear portion was measured. Using the above expression for the magnitude of this slope, S_0 could then be calculated. When no such linear portion was found, no value for the burning velocity was assigned.

It is seen from Table I that the burning velocity calculated in this manner is substantially constant over a range of flow rates and burner diameters. The notation N.V. indicates that no region of constant burning velocity was found for this flow rate. In general there was a range of flow rates between flash-back and blow-off for which a value of the burning velocity could be assigned, this range becoming smaller the lower the pressure and burner diameter.

The frustum method described by Lewis and von Elbe[6] gives an average value for the burning velocity over the portion of the flame surface considered. If the burning velocity is constant over the frustum chosen, the same result will be obtained as in the above angle method. There is a cancellation at the base and tip of the frustum of the error due to deviation of the flow lines from the vertical axis before reaching the inside edge of the visible cone.[6] Thus, this source of error will be small in either the frustum or modified angle method. If the burning velocity is not constant over the frustum chosen, the value obtained by this method may not be the true value for the mixture. In Table II

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(5) B. Lewis and G. von Elbe, "Combustion, Flames, and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1951, p. 471, *J. Chem. Phys.*, **11**, 75 (1943).

(6) Ref. 5, p. 464.

TABLE I

BURNING VELOCITIES CALCULATED BY THE MODIFIED ANGLE METHOD OF STOICHIOMETRIC CH_4–AIR (9.46% CH_4)

Flow rate, cc./sec.	Burning velocity, cm./sec.	Flow rate, cc./sec.	Burning velocity, cm./sec.
Pressure, 1 atm.			
Burner diameter = 1.603 cm.		Burner diameter = 0.896 cm.	
278.8	39.4	100.5	39.4
269.0	40.0	97.5	42.3
259.0	39.5	89.5	39.8
249.3	41.2	87.3	38.6
240.5	39.8	85.1	41.2
221.0	40.2	76.4	N.V.
210.1	39.8	69.7	N.V.
Mean value	39.9	64.6	N.V.
		59.7	N.V.
		Mean value	40.3
Pressure, $^1/_2$ atm.			
Burner diameter = 2.059 cm.		Burner diameter = 1.603 cm.	
671	N.V.	322	N.V.
555	N.V.	278.6	N.V.
437	48.2	250.8	52.1
410.7	51.8	240.5	50.8
391.0	51.9	236.2	52.0
360.3	52.8	228.6	51.0
337.5	49.5	219.1	53.1
309.0	51.8	200.2	N.V.
287.0	53.6	162.0	N.V.
258.2	51.6	Mean value	51.8
Mean value	51.4		

are tabulated burning velocities calculated by the frustum method on both visible and shadow cones for stoichiometric methane–air mixtures a $^1/_2$ atmosphere pressure. In all cases the radii of the frustum were approximately 0.16 and 0.7 *R*. With each of the three burners used there appears to be a trend toward higher burning velocities with lower flow rates. This is due to the fact that at the lower flow rates the frustum chosen over-emphasized the upper portion of the flame, thus giving a higher apparent burning velocity. The values for the 0.896 cm. diameter burner appear particularly high; however, there was no flow rate with this burner for which a region of constant burning velocity could be obtained. By choosing a different frustum the values can be brought into agreement with those obtained using the other two burners.

TABLE II

COMPARISON OF TOTAL AREA AND FRUSTUM METHODS AT $^1/_2$ ATMOSPHERE FOR 9.46% CH_4–AIR

Flow rate, cc./sec.	Burning velocity, cm./sec. Frustum visible cone	Total area shadow cone	Frustum shadow cone
Burner diameter = 2.059 cm.			
681.5	47.7	44.6	50.4
550	48.0	45.0	50.1
428	49.4	42.6	49.2
256	53.8	47.5	57.8
Burner diameter = 1.603 cm.			
321	47.9	42.2	50.0
255	47.4	41.3	50.5
193	51.2	43.7	55.9
158.1	51.1	41.4	54.9
Burner diameter = 0.896 cm.			
60.4	66.3	40.3	59.6
50.1	68.4	40.5	59.9
40.1	71.9	44.0	66.9
30.1	69.2	49.5	68.6

The total area method again gives an average burning velocity, but in this case over the entire region of the cone. It is only when the errors due to curvature and quenching cancel each other that agreement is obtained with the angle method. The values in Table II are dependent to some extent on flow rate and burner diameter and are lower than the results obtained with either the frustum or modified angle method.

Discussion of Results

The experimental results are shown in Figs. 1 and 2, all values being obtained by the modified angle method described above. In Fig. 1 a comparison is made between methane burning in N_2, A and He

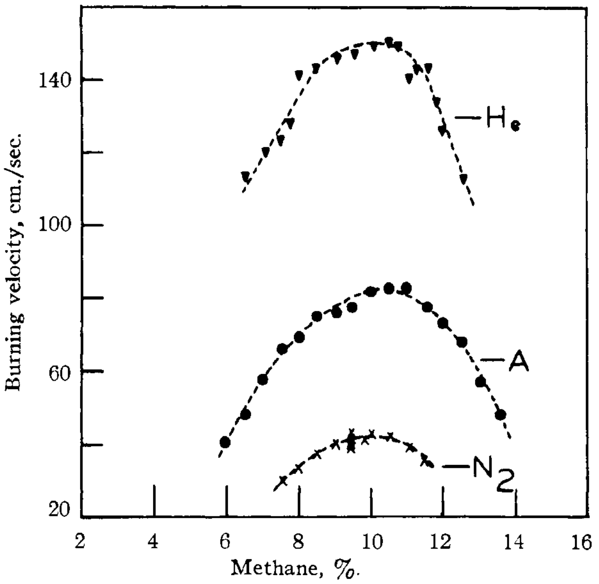

Fig. 1.—Burning velocities of methane at atmospheric pressure.

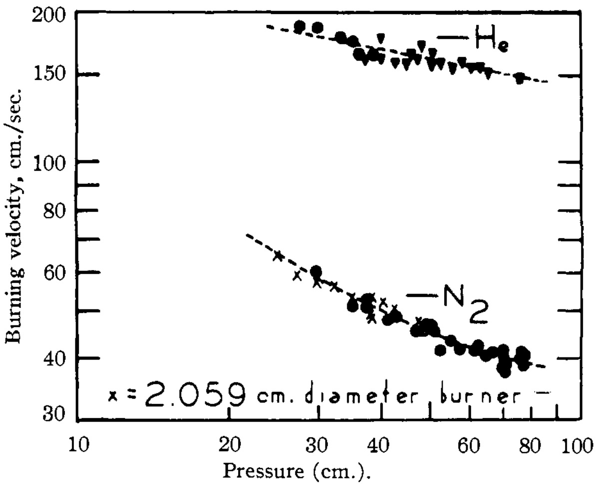

Fig. 2.—Burning velocities of stoichiometric mixtures at reduced pressures: X, 2.059 cm. diameter burner; ●, 1.603 cm.; ▼, 1.256 cm.; ■, 0.896 cm.

"airs" at atmospheric pressure. The results are somewhat different from those obtained previously[4] by using the total area method on the shadow cone, and thus are reported for the sake of completeness. The values for the He–"air" mixtures are higher while those for A–"air" near the stoichiometric composition are lower than the values previously reported.

Measurements at reduced pressures are given in Fig. 2. Near one atmosphere the burning velocity of the mixtures with N_2–"air" was found to vary as the -0.25 power of the pressure, while at one-half atmosphere the pressure exponent had decreased to -0.5. For mixtures with He-"air" the pressure exponent was -0.2. It is seen that good agreement was obtained with the different burners used.

Lewis,[7] using a spherical bomb to determine burning velocities, has obtained a pressure exponent of -0.18 for stoichiometric methane–air mixtures. On the other hand, Egerton[8] has recently found a pressure exponent of -0.5 using a tube method. If there is an error due to quenching in either the latter or our results, then the true burning velocity will rise even faster with decreasing pressure, since this error would be greater at lower pressures. It also does not seem likely that, should an error due to curvature be present in our results, it could account for the discrepancy between them and those obtained by Lewis.

The experimental burning velocities have been compared with relative theoretical values calculated using both the Semenov and Tanford–Pease treatments. In these calculations the same values for the parameters were used as previously reported[4] with the additional flame temperatures and equilibrium concentrations given in Table III for the reduced pressures.

TABLE III

FLAME TEMPERATURES AND EQUILIBRIUM ATOM AND RADICAL CONCENTRATIONS FOR STOICHIOMETRIC MIXTURES AT REDUCED PRESSURES

Pressure, atm.	Inert gas	Flame temp., °K.	Mole fraction × 10^4 H	OH	O
1	N_2	2214	3.57	27.8	2.11
3/4	N_2	2208	4.12	29.6	2.45
1/2	N_2	2200	5.01	32.9	3.08
3/8	N_2	2194	5.91	35.2	3.53
1	He	2514	26.1	100.4	19.5
3/4	He	2502	28.4	102.9	21.5
1/2	He	2478	32.6	107.1	24.2
3/8	He	2463	35.8	109.8	26.1

The Semenov equation assuming a bimolecular reaction may be written[9]

$$S_0 = \left[\frac{2\lambda\, T \int_0^{T_f} w\, dT}{a_0\, \rho_0\, c_p} \left(\frac{n_1}{n_2}\right)^m \left(\frac{\lambda}{D c_p \rho}\right)_f^m\right]^{1/2} \qquad (6)$$

where

λ = thermal conductivity
a = concn. of fuel
ρ = density
c_p = mean specific heat over the combustion wave
$\frac{n_1}{n_2}$ = moles of reactants per mole of products from stoichiometric equation
w = reaction rate
D = diffusion coefficient
m = molecularity of flame reaction
T = absolute temperature

The subscript ($_0$) refers to the initial mixture, while the subscript (f) refers to the value at the flame temperature. Simon and Dugger[9] have compared experimental values for the burning velocities of hydrocarbons with equation 6. Using the expressions which they have given for $\int_{T_0}^{T_f} w\, dT$ and the parameters of the system, (6) may be written in the following form, which applies to stoichiometric mixtures for which only the identity of the inert gas and the pressure are varied.

$$S_0 = A\, \frac{\lambda_0^{1/2} T_f^{2.37} \exp(-E/2RT_f)}{C_p^{3/2}\, (T_f - T_0)^{3/2}}\, (C_p + 5/4\, R) \qquad (7)$$

where

C_p = heat capacity
E = activation energy
R = gas constant
A = a proportionality factor

In arriving at equation 7 it was assumed that C_p is constant with respect to temperature and that λ is proportional to $T^{0.75}$.

Relative values were calculated for S_0 using an activation energy of 51 kcal.[10] and are given in Table IV. The values at the low pressures were adjusted to give agreement with the experimental value at one atmosphere. The Semenov equation does not account for the observed pressure effect on the burning velocity, predicting a decrease in burning velocity instead of an increase with a decrease in pressure. Since the reaction was assumed to be bimolecular, this is a result of the decrease in flame temperature at the reduced pressures. If the thermal model used in the derivation of the Semenov equation is to explain the results, it is necessary to postulate the existence of an important first-order chemical reaction, or an over-all reaction of fractional order.

TABLE IV

COMPARISON OF THEORETICAL AND EXPERIMENTAL BURNING VELOCITIES FOR STOICHIOMETRIC MIXTURES[a]

Pressure, atm.	Inert gas	Burning velocity, cm./sec. Exptl.	Tanford–Pease	Semenov
1	N_2	41.0	(41.0)	(41.0)
3/4	N_2	43.1	42.2	40.1
1/2	N_2	51.8	44.3	38.9
3/8	N_2	59.7	45.7	37.3
1	He	149.2	(149.2)	(149.2)
3/4	He	157.5	152.2	146.0
1/2	He	170.0	154.7	140.0
3/8	He	180.0	158.1	135.0
1	A	80.0	...	...

[a] Values in parentheses were assumed.

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(7) B. Lewis, "Remarks on the Combustion Wave," Colloquium held by the Advisory Group for Aeronautical Research and Development, North Atlantic Treaty Organization, at Cambridge, England, December 7-11, 1953.

(8) Sir A. Egerton and A. H. Lefebvre, *Proc. Roy. Soc.* (*London*), **222A**, 206 (1954).

(9) G. L. Dugger and D. M. Simon, "Fourth Symposium on Combustion," The Williams and Wilkins Company, Baltimore, Md., 1953, p. 336.

(10) G. H. N. Chamberlain and A. D. Walsh, *Rev. inst. franc. petrole Ann. combustible liquides*, **4**, 315 (1949).

The Tanford–Pease equation may be written[4]

$$S_0 = \left[\frac{0.7LT_0}{T_m}\sum_i (k_iP_iD_i)\right]^{1/2} \tag{8}$$

where

P_i = partial pressure of 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

k_i = rate constant for the reaction of the ith active species with the fuel.

In using equation 8 the active species considered were H, OH and O, a steric factor of 0.05 being used for the reaction of H with CH_4 while a steric factor of 0.1 was used for the reactions of the other two species with the fuel.

A value was assigned to T_m in the manner now to be described. Tanford[11] has derived an expression for c_i, the partial pressure of the ith active species upstream from the flame front, which may be written as

$$c_i = P_i \exp\left[\frac{S_0T_0}{D_iT_m}X\right] \tag{9}$$

where X = the distance from the flame front (negative).

The assumption has been made in deriving equation 9 that the net rate of chemical production of the ith active species is zero. Equation 9 may also be written as

$$c_i = P_i \exp y_i, \text{ where } y_i = \frac{S_0T_0}{D_iT_m}X \tag{10}$$

It was found that the experimentally determined temperature distributions of Friedman[12] for a propane–air flame (3.3% propane, pressure = 0.975 atm.) and Dixon-Lewis[13] for a methane–air flame (9.7% methane, pressure = 1 atm.) could be represented approximately in the combustion zone by the expression

$$\frac{T}{T_0} - \frac{T_f}{T_0} = \left[\frac{2\rho_0C_pD_iT_m}{3\lambda_0T_0}\right] y_i \tag{11}$$

Since Friedman[12] has shown that T/T_0 is a universal function of $(\rho_0C_pD_iT_m/\lambda_0T_0)y_i$ in the pre-heating zone where chemical heat production is small, equation 11 is essentially a dimensional relationship combined with the assumption that the temperature is a linear function of distance in the reaction zone.

Consider for the moment that there is only one active species present. Since T_m is to represent the effective temperature at which chemical reaction of that species with the fuel is taking place, it seems reasonable on considering equations 10 and 11 to choose T_m in such a way that $(T_m/T_0) - (T_f/T_0)$ is proportional to $(2\rho_0C_pD_iT_m/3\lambda_0T_0)$. T_m may then be expressed as

$$T_m = \frac{T_f}{1 - \beta\dfrac{C_pD_i}{\lambda_0T_0}} \tag{12}$$

where β is a proportionality constant.

For the case of several active species, D_i may be replaced by an average diffusion coefficient, $\bar{D}$, defined as $\bar{D} = \sum_i P_iD_i/\sum_i P_i$. Equation 12 then becomes

$$T_m = \frac{T_f}{1 - \beta\dfrac{C_p\bar{D}}{\lambda_0T_0}} \tag{13}$$

β was chosen in the present investigation so that $T_m/T_f = 0.7$ for a stoichiometric methane–air flame at atmospheric pressure.

Relative values calculated using equation 8 are given in Table IV. Although an increase in burning velocity with decreasing pressure is predicted by the Pease–Tanford equation, this increase is not as large as that observed experimentally. Qualitative agreement between the N_2–"air" and He–"air" mixtures is obtained, however, in that the observed pressure exponent is more negative with the N_2–"air," as predicted by the theory.

One of the main assumptions in the derivation of (8) is that the net chemical production of active species or chain carriers is set equal to zero, which is equivalent to the statment that chain branching is equal to chain ending. Penner and Von Karman[14] have made a similar hypothesis with respect to oxygen atoms in their treatment of the ozone decomposition flame. Good agreement, provided the chemical assumptions are correct, might be expected between relative calculated and experimental values where pressure is the only variable, since other parameters such as the flame temperature change only slightly. If second-order chain branching and third-order chain ending reactions occur to a significant extent, then although there may be no net production of a chain carrier at one atmosphere, the chemical production of the species will increase with decreasing pressure. The effective concentration of active species in the combustion zone would thus be greater than that calculated at the subatmospheric pressures and could account for the observed rise in burning velocity. Tanford and Pease[2] considered third-order recombination of H atoms, but these reactions are too slow at the H atom concentrations considered to affect the results appreciably. If chain branching is present, however, the concentration of any active species in the combustion zone may well be above the equilibrium concentration in the burner gas, thus increasing the importance of third-order recombinations.

Although a thermal model of the combustion wave does not explain our results, we feel that the thermal conductivity of the mixture is important in that it affects the mean temperatures at which the flame reactions take place. Of the Tanford–Pease and Semenov treatments, the former is in better agreement with the results we have obtained at reduced pressures. To explain fully the effect of pressure on burning velocity, however, it is necessary to postulate that chain-branching and chain-

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(11) C. Tanford, *J. Chem. Phys.*, **15**, 433 (1947).

(12) R. Friedman, "Fourth Symposium on Combustion," The Williams and Wilkins Company, Baltimore, Md., 1953, p. 259.

(13) G. Dixon-Lewis, ref. 12, p. 263.

(14) T. Von Karman and S. S. Penner, "Fundamental Approach to 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.

ending processes are important in the combustion wave. Further discussion of these reactions is postponed until more is known about the chemistry of methane oxidation at the high temperatures present in flames.

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[CONTRIBUTION FROM THE EXPLOSIVES RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE LABORATORY]

The Thermal Decomposition of Ethyl Nitrite[1,2]

BY JOSEPH B. LEVY

RECEIVED OCTOBER 21, 1955

The thermal decomposition of ethyl nitrite has been investigated in the gas phase at pressures of 10–50 mm. and temperatures of 161, 181 and 201°. Reaction kinetics have been measured and reaction products analyzed by means of the infrared spectra. Nitrous oxide, acetaldehyde, ethyl alcohol and nitric oxide have been found as products. The yields of acetaldehyde ranged from 60–90%. The addition of large amounts of nitric oxide did not materially affect the reaction rate but boosted the acetaldehyde yield toward a limit of 100% and the nitrous oxide yield to 50%. In the presence of added acetaldehyde the rate increased sharply and nitrous oxide was not a product. A mechanism has been suggested to explain these results.

Introduction

The thermal decomposition of nitrite esters has been the subject of much study[3–7] and has generally been discussed in terms of the following mechanism, written for the ethyl nitrite case, and referred to hereafter as the Steacie–Rice mechanism.

$$C_2H_5ONO \underset{k^{-1}}{\overset{k_1}{\rightleftarrows}} C_2H_5O\cdot + NO$$

$$C_2H_5O\cdot + C_2H_5ONO \xrightarrow{k_2} C_2H_5OH + CH_3\cdot CHONO$$

$$CH_3\underset{\cdot}{C}HONO \longrightarrow CH_3CHO + NO$$

$$C_2H_5O\cdot \longrightarrow CH_3\cdot + CH_2O$$

$$CH_3\cdot + C_2H_5ONO \longrightarrow CH_4 + CH_3\underset{\cdot}{C}HONO$$

The decomposition reactions have generally been studied kinetically in the temperature range 160–220°. Evidence for the last two steps has been found at temperatures of about 400° and at very low pressures.[4] At the lower temperatures only the first three steps appear to be important. To satisfy the observed first-order kinetics it is necessary in considering these steps to assume that $k_2 >> k_{-1}$. Evidence recently has been found in this Laboratory that not only contradicts this assumption but also indicates that the second step plays no role in the reaction.[8] The thermal decomposition of ethyl nitrite has accordingly been investigated in the temperature range 161–201° at pressures of the order of 10–50 mm. The analytical tool used has been the infrared spectrometer. The results are reported below.

Experimental Part

Chemicals.—The ethyl nitrite was prepared in standard fashion,[3a] distilled and a middle fraction taken. It was stored in sealed ampules in a refrigerator.

In the early experiments the nitric oxide used was purchased from the Matheson Company. It was condensed into a tube on the vacuum line. By warming the tube only slightly it was possible to generate nitric oxide free of nitrogen dioxide. Small amounts of nitrous oxide were observed at times in the nitric oxide, however, and when it became clear that nitrous oxide was a product in some of the decompositions, a different source of nitric oxide was used. This involved the preparation of nitric oxide from potassium nitrate, sulfuric acid and mercury. No nitrous oxide was ever observed in this nitric oxide. This latter source of nitric oxide was used where analyses for nitrous oxide were made.

Acetaldehyde used was Eastman Kodak White Label grade and was taken directly from the bottle. Ethyl alcohol was 100% ethanol U.S.P. grade. The nitrous oxide used was taken directly from the cylinder.

The Analytical Procedure.—The compounds considered in setting up the analytical scheme were ethyl nitrite itself, acetaldehyde and nitrous oxide. Nitric oxide and ethanol were omitted because no suitable peaks for them are available in the infrared region involved.

Ethyl nitrite and acetaldehyde were determined using their absorption peaks at 12.85 and 5.70 μ, respectively. The analysis for nitrous oxide is more difficult because the intensity of the absorption peaks is not independent of the total pressure.[9] For this reason it was necessary to set up a calibration curve using some standard total pressure. The wave length used was 4.50 μ and the total pressure was set at atmospheric and was attained merely by opening the cell stopcock to the air.

The analysis for these three compounds was tested using synthetic mixtures containing all the products, *viz.*, ethyl nitrite, acetaldehyde, nitrous oxide and nitric oxide in amounts corresponding to various stages of reaction. The results indicated that ethyl nitrite, acetaldehyde and nitrous oxide could be determined to ±0.3 mm. In the actual analysis of decomposition runs the procedure was first to analyze for the ethyl nitrite and acetaldehyde. The stopcock to the infrared cell was then opened to the atmosphere and closed and the optical density at the nitrous oxide peak taken.

Results

The Nature of the Products.—Figure 1 is the spectrum of a sample of ethyl nitrite carried to complete decomposition. Acetaldehyde may be identified by the carbonyl absorption at 5.65 μ and the characteristic aldehyde C–H absorption at 3.5–3.75 μ. The presence of ethyl alcohol is best established by admitting air to the infrared cell. As shown in Fig. 1 this results in the appearance of the ethyl nitrite spectrum coupled with a decrease in the absorption at 9.4 μ, where C–O absorption peak of ethyl alcohol is found. This last peak is not

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[1] The material reported here was presented in part before the Division of Physical and Inorganic Chemistry at the 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954.

[2] Full experimental details of this work, including infrared spectra can be found in the reference, J. B. Levy, NavOrd 3833, 1954.

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