Kinetic Parameters for the Hydrogen and Ethylene Flames from Flashback Measurements

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(*Received May 1959*)

Values for the flame activation energy and an overall reaction order have been obtained for premixed hydrogen–oxygen and ethylene–oxygen flames with nitrogen and with argon as diluents; the values come from measurements of the change with pressure and flame temperature of the critical boundary velocity gradient for flashback. Measurements have been made for rich and stoichiometric hydrogen flames and for lean and stoichiometric ethylene flames. For hydrogen flames with nitrogen diluent an overall order of 2·3 is found; for ethylene flames with nitrogen diluent, the order obtained is 1·8. With argon diluent, values for the order are about 10 per cent lower for each flame. With nitrogen diluent the flame activation energy apparently increases with flame temperature; this increase is not found with argon diluent. For hydrocarbon flames the assumption that the initial equivalence ratio equals the effective equivalence ratio in the flame leads to an order of reaction with respect to oxygen that is considerably larger than unity. For hydrogen flames, that assumption is consistent with an oxygen order of unity.

Introduction

IN SEVERAL previous studies, the change of various properties of burner flames with pressure as been related to an overall order for the hemical reaction taking place within the lame[1, 2]. Frequently, the pressure dependence f the flame property increased with flame emperature. Thus, if one assumed that the lame reaction was described by a constant ctivation energy, the overall order likewise ncreased with flame temperature.

The present study is an attempt to examine n greater detail this apparent change of reaction rder with flame temperature through measurement of the flashback of laminar burner flames. Measurements have been made with independent variation of pressure and flame temperature. This should permit a simultaneous determination f the overall order and activation energy for a lame reaction involving fuel and oxygen. In ddition flashback measurements with variation f equivalence ratio have been made in an ttempt to determine orders with respect to ndividual components of the initial mixture. Data are presented for premixed hydrogen–xygen and hydrocarbon–oxygen flames with itrogen, with argon, and with helium as iluents.

Theoretical Background

The critical boundary velocity gradient for flashback, g, has often been related to ϖ, the mean flame reaction rate, by the relation[1, 3]

$$ga \propto \varpi \qquad \dots . [1]$$

where, for lean and stoichiometric flames, a is the volume concentration of fuel in the initial mixture and ϖ is defined as

$$\frac{1}{(T_f - T_0)} \int_{T_0}^{T_f} \omega \, \mathrm{d}T$$

where T_f is the flame temperature and T_0 the initial gas temperature. Within the approximation of equation1, g gives a measure of ϖ independent of transport processes within the flame. Thus, if equation 1 is valid, the change of g with various experimental conditions should be related in a particularly simple fashion to the various parameters describing the flame reaction.

One may assume[4] that the mean flame reaction rate can be represented as

$$\varpi = k\mathbf{a}_1^m \mathbf{a}_2^n \mathbf{a}_3^l F_{\text{III}}(T_f) \qquad \dots [2]$$

where $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are, respectively, the effective volume concentrations of fuel, oxygen and diluent in the flame zone, k is a constant and F_{III} is some function of flame temperature. The fact that ϖ depends on initial temperature as well as flame temperature will be neglected here. In terms of mole fractions, x_i, equation 2 can be written as

$$\varpi = k'\mathbf{x}_1^m \mathbf{x}_2^n \mathbf{x}_3^l P^{m+n+l} F_{II}(T_f) \quad \ldots . [3]$$

where P is pressure and F_{II} is another function of flame temperature. If one combines equations 1 and 3 and introduces the equivalence ratio

$$\phi = (x_1/x_2)/(x_1/x_2)_{\text{stoich.}} \quad \ldots . [4]$$

one obtains

$$g \propto \mathbf{x}_1^{m+n} \mathbf{x}_3^l \mathbf{x}_1^{-1} (\phi)^{-n} T_0 P^{m+n+l-1} F_I(T_f) \quad . [5]$$

For any reactant whose proportion in the initial mixture is equal to or less than stoichiometric, the effective mole fraction, $\mathbf{x}_i$, will be proportional to the initial mole fraction x_i, differing by a factor of order of magnitude

$$(RT_f^2/E)/(T_f - T_0)$$

where E is an activation energy for the overall flame reaction[4]. For a reactant whose proportion in the initial mixture is greater than stoichiometric, the initial and effective mole fractions can be related by expressions of the form

$$\begin{aligned} \mathbf{x}_2 &= x_2 - \delta_2 x_1 \quad (\phi < 1) \\ \mathbf{x}_1 &= x_1 - \delta_1 x_2 \quad (\phi > 1) \end{aligned} \quad \ldots . [6]$$

where the δs describe the depletion of fuel or oxygen due to reaction in the flame zone[3]. Then the change of flashback gradient with, for example, oxygen concentration can be represented as

$$g \propto (x_2 - \delta_2 x_1)^n \quad (\phi < 1) \quad \ldots . [7]$$

If either δ_2 or the range of variation of x_2 is not too large, equation 7 can be approximated by

$$g \propto (x_2)^{n'} \quad \ldots . [8]$$

If δ_2, in addition to being reasonably small, is also positive, then $n' > n$. By use of equation 8, equation 5 can be written in terms of initial mole fractions as

$$g \propto x_1^{m+n-1} x_3^l (\phi)^{-n'} T_0 P^{m+m+l-1} F(T_f) \quad . [9]$$

Thus, the relation between n', an empirically determined exponent, and n, the order of reaction with respect to oxygen, depends on the relation between the initial equivalence ratio and the effective equivalence ratio in the flame zone.

Equation 9 applies only to lean and stoichiometric flames. However, one may derive an equation analogous to equation 9 for rich or stoichiometric flames. The result is

$$g \propto x_2^{m+n-1} x_3^l (\phi)^{m'} T_0 P^{m+n+l-1} F(T_f) \quad . . [10]$$

Here, m' is another empirical constant related in some fashion to the fuel order m, depending on the relation between initial and effective equivalence ratios.

If one defines the overall reaction order as

$$r = l + m + n \quad \ldots . [11]$$

then, for a given initial mixture, equations 9 or 10 can be written as

$$g \propto P^{r-1} F(T_f) \quad \ldots . [12]$$

Logarithmic differentiation with respect to pressure gives

$$\frac{\mathrm{d} \log g}{\mathrm{d} \log P} = (r-1) + \frac{\mathrm{d} \log F(T_f)}{\mathrm{d} \log P} \quad \ldots . [13]$$

in which the last term is generally a small correction. Equation 13 in turn can be written

$$\frac{\mathrm{d} \log g}{\mathrm{d} \log P} = (r-1) + \left[\frac{\partial \log F(T_f)}{\partial \log T_f}\right]_P \frac{\mathrm{d} \log T_f}{\mathrm{d} \log P} \quad . [14]$$

in which $[\partial \log F(T_f)/\partial \log T]_P$ depends on the flame temperature and activation energy E. According to the thermal quenching theory of A. E. POTTER, Jr and A. L. BERLAD[2] that derivative can be set approximately equal to $1{\cdot}125\, E/RT_f$. In order to evaluate the two unknowns r and $[\partial \log F(T_f)/\partial \log T_f]_P$ in equation 14, one needs independent determination of the change of g with pressure and flame temperature.

Expressions for the change of g with flame temperature can be obtained from consideration of equations 9 and 10. Thus, if $l=0$ (that is, the reaction does not depend on inert constituents) the quantity

$$Y_1 = g\phi^{n'} x_1^{1-r} T_0^{-1}$$

should depend on flame temperature alone for lean and stoichiometric flames. For rich and stoichiometric flames, the quantity

$$Y_2 = g\phi^{-m'} x_2^{1-r} T_0^{-1}$$

should have the same dependence on flame temperature. These correlating functions Y_1 and Y_2 are similar in form to those devised by R. S. Brokaw and M. Gerstein[5] for correlating burning velocity, quenching distance and minimum ignition energy with flame temperature. Then, if g is obtained experimentally at constant pressure, a plot of either Y_1 or Y_2 against T_f^{-1} should give an activation energy and a value of $[\partial \log F(T_f)/\partial \log T_f]_P$. However, the value of r used in the correlation must be consistent with equation 13. Since r is unknown, both r and $[\partial \log F(T_f)/\partial \log T_f]_P$ must be obtained in some simultaneous fashion. The resulting values of the overall order will be largely independent of the aforementioned assumption that $l=0$, since that assumption affects only the small correction term in equations 13 or 14.

Experimental

The gas metering system, low-pressure combustion chamber and procedure for producing flashback have been described previously[1, 6]. The main burner was a brass tube, 125 cm long and 1·89 cm in diameter which was water-cooled near the lip. In the present study, burner diameter was varied by using inserts 0·928, 1·016 and 1·459 cm in diameter.

Hydrogen (98–99 per cent H_2) and technical grade ethylene (95 per cent C_2H_4) were used as fuels. Oxidant mixtures were prepared by separately metering the flow of oxygen and diluent and mixing the flowing gases or were commercially prepared. All gases were obtained from tanks and used without further purification.

The critical boundary velocity gradient for flashback was computed as

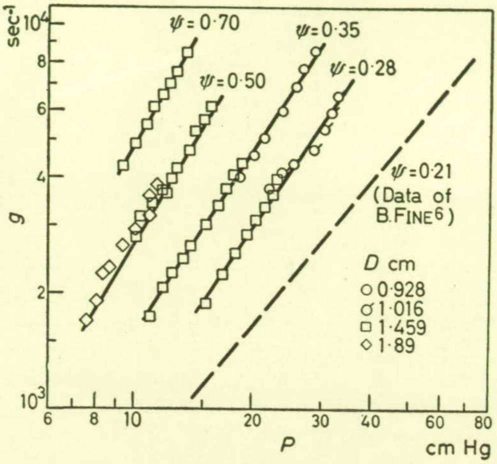
$$g = 8\bar{U}/D$$

where $\bar{U}$ is the mean stream velocity at flashback and D the burner diameter[7].

Results

Description of results

Figures 1 to *4* show log g plotted against log pressure for stoichiometric hydrogen–oxygen–nitrogen flames (*Figure 1*), rich and stoichiometric hydrogen–oxygen–argon flames (*Figure 2*), lean and stoichiometric ethylene–oxygen–nitrogen flames (*Figure 3*) and lean and stoichiometric ethylene–oxygen–argon flames (*Figure 4*).



Figue 1. Flashback of stoichiometric H_2–N_2–O_2 *flames*

Figure 3 contains, in addition, results obtained by J. E. Garside, J. S. Forsyth, and D. T. A. Townend[8] for stoichiometric ethylene–air flames. The higher values obtained in their study may be a result of their having used a burner whose lip was not cooled. One curve in *Figure 4* involves the use of helium rather than argon as diluent. However, it was established previously[1] that substitution of helium for argon did not change the critical flashback gradient.

Compositions of the various initial mixtures are designated by the equivalence ratio, ϕ, defined in equation 4 and the oxidant strength ψ defined as

$$\psi = x_2/(x_2 + x_3)$$

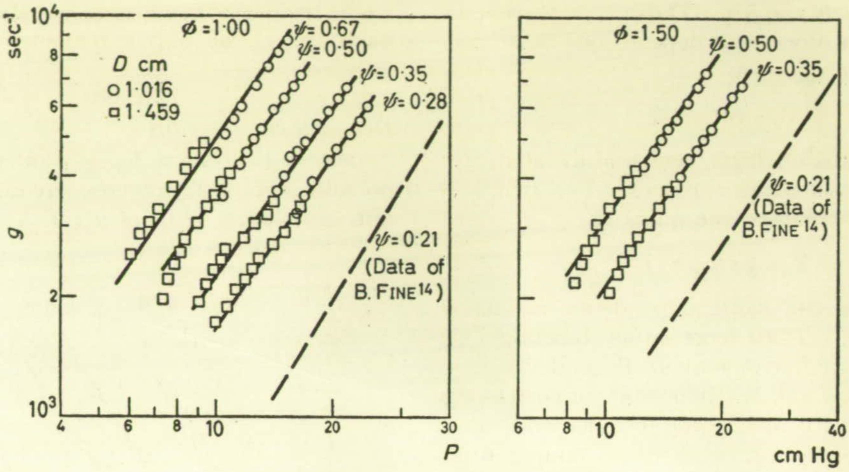


Figure 2. Flashback of H_2–O_2–A *flames*

Log-log pressure slopes, obtained from the data of *Figures 1* to *4*, are presented in *Tables 1* and *2*. They are given to two decimal places, although the significance of the second place is somewhat doubtful. Also shown in *Tables 1* and *2* are flame temperatures, calculated from a self-consistent set of thermal data by the method of ref. 9. Values shown for d log T_f/d log P are based on flame temperatures at 1 and 0·1 atmosphere.

It can be seen from *Figures 1* to *4* that critical flashback gradients are always independent of burner diameter where argon is used as diluent. A few exceptions have been found, however, with nitrogen as a diluent. For lean ethylene flames (*Figure 3*) at an oxidant strength of 0·67, values of g at constant pressure decreased with decreasing burner diameter even for the two largest burners available. The magnitude of the decrease was about 20 per cent. In

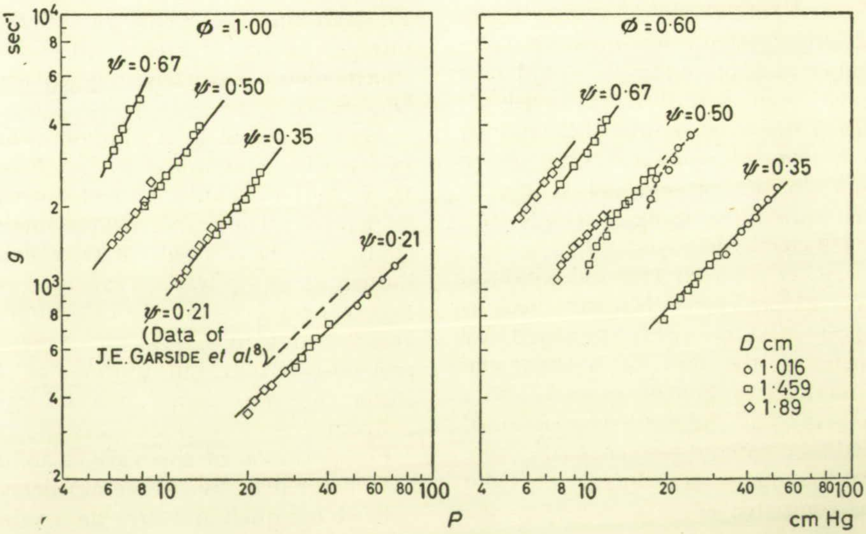


Figure 3. Flashback of C_2H_4–O_2–N_2 *flames*

Table 1. Correlation of critical flashback gradient g with flame temperature for hydrogen–oxygen flames; pressure, 15 cm of mercury

ψ	ϕ	*Diluent*	x_2	T_0 °*K*	T_f °*K*	$\frac{10^4}{T_f}$ °*K*$^{-1}$	$\frac{\text{d} \log T_f}{\text{d} \log P}$	*g* *sec*$^{-1}$	$\frac{\text{d} \log g}{\text{d} \log P}$	*r*	*m′*	*Source of g*	$\left[\frac{\partial \log F(T_f)}{\partial \log T_f}\right]_P$
0·21	1·50	N_2	0·129	298	2 230	4·484	0·0120	1 500	1·35		1·32	*Ref. 1*	—
0·21	1·00		0·148	298	2 322	4·307	0·0157	1 140	1·35	2·28	—	*Ref. 6*	3·4
0·21	1·50		0·129	659	2 430	4·115	0·0184	4 800	ca. 1·4		1·18	*Ref. 10*	—
0·28	1·00		0·180	298	2 500	4·000	0·0209	1 880	1·54	2·43		*This work*	5·3
0·28	1·60		0·148		2 371	4·218	0·0172	2 160	1·33		1·16	*Ref. 3*	—
0·35	1·00		0·205		2 602	3·843	0·0298	2 930	1·55	2·35	—	*This work*	6·8
0·49	1·44		0·205		2 691	3·716	0·0327	4 800	1·55		0·69	*Ref. 3*	—
0·50	1·00		0·250		2 726	3·668	0·0355	5 450	1·72	2·31	—	*This work*	11·4
0·70	↓	↓	0·292	↓	2 809	3·560	0·0391	10 000	1·79	2·21	—	*This work*	14·9
0·21	1·00	A	0·148	298	2 527	3·957	0·0275	1 300	1·50	2·24	—	*Ref. 14*	9·6
0·21	1·50		0·129		2 467	4·053	0·0207	1 750	1·49			*Ref. 14*	—
0·28	1·00		0·180		2 631	3·801	0·0326	2 930	1·44	2·14	—	*This work*	9·3
0·35	1·00		0·205		2 695	3·711	0·0351	3 910	1·40	2·09	—		9·0
0·35	1·50		0·171		2 652	3·771	0·0312	3 800	1·46		0·92		—
0·50	1·00		0·250		2 774	3·605	0·0383	6 200	1·39	2·13	—		8·8
0·50	1·50		0·200		2 725	3·670	0·0335	5 600	1·43		0·74		—
0·67	1·00	↓	0·285	↓	2 824	3·541	0·0399	8 875	1·50	2·16	—	↓	8·6

accordance with the conclusions of a previous discussion[3] of this effect only data for the larger of the two burners ($d = 1{\cdot}89$ cm) are used in the calculations which follow. For an oxidant strength of 0·50, results are complicated by partial quenching at low Reynolds numbers. However, at sufficiently high Reynolds numbers, it is seen that critical flashback gradients are still somewhat dependent on burner diameter, decreasing slightly with decreasing burner size. For stoichiometric ethylene and hydrogen flames with nitrogen diluent, at oxidant strengths near 0·7, data were obtained in only one burner. It is possible then that these values are too low by 20 per cent or more. This could not be checked because bigger burners could not be used.

Usually the log-log pressure slopes are constant for any single initial mixture. The most pronounced exception is noted in *Figure 3* where quenching at low Reynolds numbers apparently affected the results for $\psi = 0{\cdot}50$ and $\phi = 0{\cdot}60$.

Table 2. Correlation of critical flashback gradient g with flame temperature for hydrocarbon–oxygen flames; pressure 10 cm of mercury

ψ	ϕ	*Fuel*	*Diluent*	x_1	T_0 °*K*	T_f °*K* (10 *cm* Hg)	$\frac{10^4}{T_f}$ °*K*$^{-1}$	$\frac{\text{d} \log T_f}{\text{d} \log P}$	*g* *sec*$^{-1}$	$\frac{\text{d} \log g}{\text{d} \log P}$	*r*	*n′*	*Source of g*	$\left[\frac{\partial \log F(T_f)}{\partial \log T_f}\right]_P$
0·21	1·00	C_2H_4	N_2	0·0654	298	2 291	4·365	0·0165	180	0·92	1·81	—	*This work*	3·4
0·21				↓	615	2 400	4·165	0·0209	550	1·0	1·81		*Ref. 15*	9·1
0·35				0·104	298	2 586	3·867	0·0294	950	1·19	1·79	—	*This work*	14·1
0·50				0·143		2 728	3·664	0·0340	2 690	1·31	1·69	—		18·3
0·67	↓			0·182		2 811	3·557	0·0391	8 300	2·07	—	—	↓	—
0·50	0·80			0·118		2 664	3·754	0·0331	2 250	1·14	1·63	1·74	*Ref. 10*	15·6
0·35	0·60			0·0654		2 331	4·290	0·0153	420	1·02	1·91	1·45	*This work*	7·4
0·50				0·0909		2 552	3·949	0·0270	1 540	ca. 1·1	1·78	1·82		11·8
0·67	↓	↓		0·118		2 675	3·738	0·0331	3 940	1·31	1·74	1·76	↓	17·1
0·50	1·00	C_3H_8	↓	0·0909		2 691	3·716	0·0250	1 400	1·15	1·73	—	*Ref. 1*	17·1
1·00	0·85	↓	O_2	0·145	↓	2 829	3·534	0·0406	5 000	1·40	—	—	*Ref. 1*	—
0·21	1·00	C_2H_4	A	0·0654	298	2 512	3·981	0·0286	339	1·07	1·63	—	*This work*	15·6
0·35				0·104		2 682	3·729	0·0352	1 500	1·07	1·56	—		14·6
0·50				0·143		2 782	3·595	0·0386	3 230	1·11	1·57	—		14·1
0·67	↓			0·182		2 843	3·517	0·0407	6 050	1·09	1·54	—		13·9
0·50	0·50			0·0770		2 563	3·902	0·0292	1 370	1·05	1·59	1·31		15·9
0·67	0·70	↓	↓	0·128	↓	2 767	3·614	0·0377	4 450	1·08	1·54	1·38	↓	14·3

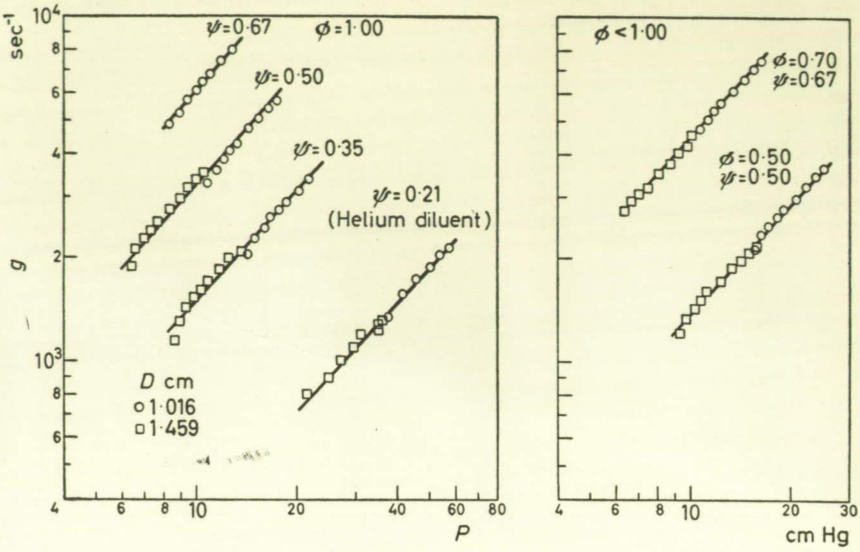


Figure 4. Flashback of C_2H_4–O_2–A *flames*

It should be noted that, with nitrogen as diluent, pressure slopes increase significantly for both hydrogen and ethylene flames with increasing levels of flame temperature. This is the effect which had been previously observed in a less systematic fashion[1]. With argon as diluent, however, no progressive change is found in the pressure slopes with flame temperature or equivalence ratio. The pressure slopes appear to depend only on the fuel type, being larger for hydrogen flames than for ethylene flames.

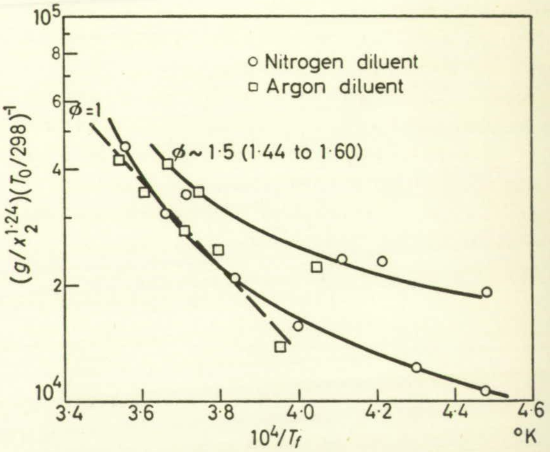


Figure 5. Correlation of g with flame temperature for rich and stoichiometric hydrogen–oxygen flames

Results for hydrogen flames

Table 1 shows values of g taken from *Figures 1* and *2* at a pressure of 15 cm of mercury; also shown are corresponding values of initial oxygen mole fraction and of flame temperature. The data include stoichiometric flames and flames near an equivalence ratio of 1·5. *Figure 5*, in turn, shows a plot against $1/T_f$ of

$$\log\left[g(T_0/298)^{-1}x_2^{1-r}\right]$$

This quantity represents either of the correlating functions Y_1 or Y_2 for stoichiometric flames. As an approximation for r, 2·24 was chosen. This is about the value obtained from the variation with pressure of flashback, burning velocity or quenching distance for hydrogen–air flames[1]. It is seen that the stoichiometric points lie on a smooth curve independent of the diluent, with the possible exception of the point for $\psi=0{\cdot}21$ with argon as diluent; this point is low by about 10 per cent. The data on the rich side describe a second curve which lies above the first and is likewise roughly independent of the diluent. The displacement of the rich points from the stoichiometric curve should permit determination of m' in the correlating function Y_2. Values obtained for each rich point are shown in *Table 1*. The values of m' are not constant, but decrease with increasing flame temperature; this is a consequence of the fact that the two curves are not parallel. Thus, the increase in $\log[g(T_0/298)^{-1}x_2^{1-r}]$ with equivalence ratio agrees only qualitatively with the prediction of theory. The failure to obtain a constant value of m' must be attributed to an error either in applying the theory or, possibly, in calculating flame temperatures. There is no likely justification for citing the results as evidence either for a change of reaction order with respect to hydrogen or a change in the degree of depletion of hydrogen in the flame zone with temperature.

It is apparent that both plots in *Figure 5* show much curvature, considerably more than can be accounted for by pre-exponential terms in $F(T_f)$. One interpretation of this curvature would be that the flame activation energy increases with flame temperature. However, at least for flames with nitrogen as diluent, one may relate the curvature in the plots against $1/T_f$ and the change of pressure slope with flame temperature. Thus, in *Figure 5*, for stoichiometric flames, one may take slopes along the appropriate curve and evaluate rough but adequate values of $[\partial \log F(T_f)/\partial \log T_f]_P$ for any value of T_f. These values are shown in *Table 1* for stoichiometric hydrogen–oxygen–nitrogen flames. When these values are used in equation 14, they permit determination of a better set of approximations to r. These values, given in *Table 1*, show no trend with flame temperature and average about 2·3. This value is sufficiently close to the original assumed value (2·24) that no further approximation is necessary.

Although the data with argon and with nitrogen as diluents generally correlate well, there is no real evidence that the argon data, as plotted in *Figure 5*, will show curvature when considered alone. This situation is somewhat indeterminate because the range of flame temperatures covered with argon as diluent is much smaller than that with nitrogen. However, if we admit that the point for $\psi=0{\cdot}21$ with argon as diluent does lie significantly below the stoichiometric nitrogen curve, then all five stoichiometric points with argon as diluent are adequately described by a straight line corresponding to an activation energy of 43 kcal/mole. Since $[\partial \log F(T_f)/\partial \log T_f]_P \approx 1{\cdot}125E/RT_f$, one may use equation 14 to obtain a set of values for r. As shown in *Table 1*, these are independent of flame temperature and average $r=2{\cdot}15$. The small difference in overall order between flames with nitrogen and those with argon as diluents is probably due to over-simplification in application of the theory.

Since the plots of $\log[g(T_0/298)^{-1}x_2^{1-r}]$ against $1/T_f$ are not parallel with change of equivalence ratio, the slopes will depend on equivalence ratio as well as on flame temperature. Therefore, unless there is some compensating change in $d \log T_f/d \log P$, the value of r will depend on equivalence ratio. In practice, however, no significant change in overall order is found between equivalence ratios of unity and about 1·5.

In summary, then, flashback data for stoichiometric hydrogen–oxygen–argon flames are described by a constant activation energy and a constant overall order based on a pressure slope for the critical flashback gradient which is independent of flame temperature. The use of nitrogen as diluent gives a variable pressure slope and an apparently variable activation energy whose effects combine to give a constant overall order.

Results for ethylene flames

Table 2 shows values of g taken from *Figures 3* and *4* at a pressure of 10 cm of mercury. Also shown are corresponding values of initial mole fraction of fuel and flame temperature. The range of data includes stoichiometric and lean ethylene–oxygen flames with nitrogen and argon diluents. It also includes results for propane–oxygen–nitrogen flames taken from ref. 1 and for ethylene–air flames at elevated initial temperature taken from ref. 10. The data shown in *Table 2* are plotted in *Figure 6* as the correlating function Y_1 against $1/T_f$. As a first approximation, it was assumed that $r=2$.

Values of n' were obtained in the same way that values of m' were obtained for hydrogen flames. The quantity $(g/x_1)(T_0/298)^{-1}$ was plotted against $1/T_f$. Then values of n' were determined so that results for lean flames fell on the curve described by the results for stoichiometric flames.

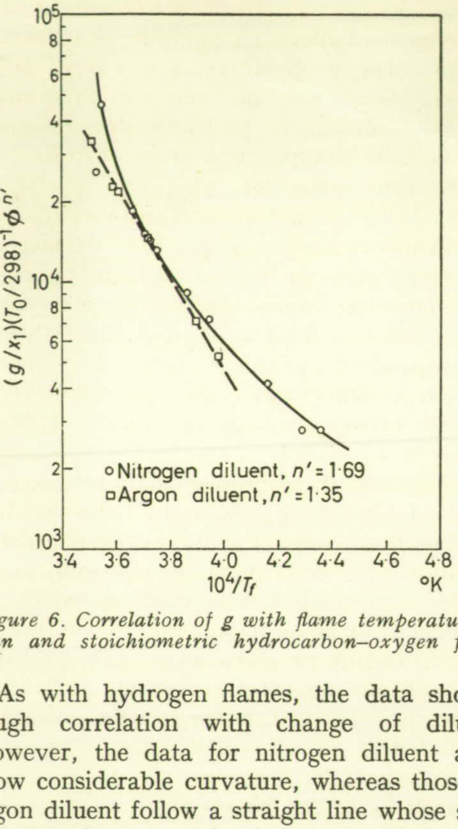


Figure 6. Correlation of g with flame temperature for lean and stoichiometric hydrocarbon–oxygen flames

As with hydrogen flames, the data show a rough correlation with change of diluent. However, the data for nitrogen diluent alone show considerable curvature, whereas those for argon diluent follow a straight line whose slope corresponds to an activation energy of about 70 kcal/mole. This behaviour is similar to that found for hydrogen flames.

The point for stoichiometric propane–oxygen–nitrogen with $\psi = 0{\cdot}50$ falls in line with the data for ethylene flames; this suggests that the correlation may be more or less general for hydrocarbon flames. However, the point for propane–oxygen ($\psi = 1{\cdot}00$) at an equivalence ratio of 0·85 falls considerably below the nitrogen curve. The reason for this is not known.

Values obtained for n' are shown in *Table 2.* The values obtained with nitrogen as diluent are reasonably constant and average **1·69**; the two values obtained with argon diluent are quite close to each other and average **1·35**. Thus, the behaviour of hydrocarbon flames with change of equivalence ratio is much simpler than for hydrogen flames.

With nitrogen diluent the plot against $1/T_f$ for hydrocarbons shows about the same degree of curvature as that for the hydrogen data. The fact that, for a given flame temperature, $[\partial \log F(T_f)/\partial \log T_f]_P$ is actually greater for hydrocarbon than for hydrogen flames is consistent with the usual observation that apparent activation energies are greater for hydrocarbon flames than for hydrogen flames. By evaluating slopes at given values of T_f and using equation **14**, one may once again obtain a set of good approximations to r. These are shown in *Table 2.* (No orders were calculated at the highest temperatures, since the slope of the curve was too large to permit evaluation of

$$[\partial \log F(T_f)/\partial \log T_f]_P$$

with any accuracy.) The values obtained average 1·77 and show no trend with temperature. This average value agrees well with values estimated from other flame properties[5, 11].

For argon diluent, the computation of

$$[\partial \log F(T_f)/\partial \log T_f]_P$$

in the determination of the overall order is based on the straight line through the corresponding data and the assumption that

$$[\partial \log F(T_f)/\partial \log T_f]_P \approx 1{\cdot}125E/RT_f$$

The values obtained for r shown in *Table 2* average 1·57, independent of flame temperature. Thus, for both hydrogen and hydrocarbon flames, the value obtained for the overall reaction order is slightly less with argon as diluent than with nitrogen.

In summary, several points of similarity are found in the correlation of critical flashback gradients with pressure and flame temperature for hydrogen and hydrocarbon flames. For both flames with nitrogen as diluent, the log-log pressure slope of the critical flashback gradient increases with flame temperature. This increase is offset by a corresponding increase in the apparent activation energy, so that the overall order is independent of flame temperature. For both flames with argon as diluent, the log-log pressure slope and apparent activation energy are independent of flame temperature and yield an overall order which is likewise constant. The orders obtained with argon as diluent are about 10 per cent lower than those with nitrogen as diluent.

Discussion of Results

Comparison with other data

The most striking result of treating flashback data in terms of a Semenov-type theory is the apparent increase of the flame activation energy with temperature for flames diluted with nitrogen. It is of interest, then, to see whether data for other properties of burner flames yield such a result when treated in a similar way. Correlations of burning velocity for hydrocarbon–oxygen–nitrogen flames reported by R. S. BROKAW and M. GERSTEIN[5] and by E. S. GOLOVINA and G. G. FYODOROV[12] show no curvature; the quenching distance correlation of Brokaw and Gerstein likewise shows no curvature. Thus the curvature appears to be specific to flashback measurements with certain diluents which include nitrogen but not argon or helium.

The activation energies obtained with argon as diluent are about twice as large as those generally assumed or determined from other properties of flames with nitrogen as diluent[12]. Since burning velocity and quenching distance have not been measured over a large range of flame temperature with argon as diluent, direct comparison is not possible in this case.

Significance of m' and n' values

In a previous report[3] values of m', n' and r were obtained for hydrogen–oxygen–nitrogen flames. The value of r was obtained from the same data and in almost the same manner as in this article. However, in that report n was obtained by observing the change of g as nitrogen was progressively replaced by oxygen at a constant lean mole fraction of hydrogen. It was found that the flame temperature changed by less than 50°K between $\phi = 1{\cdot}00$ and $\phi = 0{\cdot}35$. A recalculation of flame temperatures in terms of more recent thermal data has yielded values which vary by less than 30°K over that range of composition. The value previously obtained for n', 0·92, suggested that the order with respect to oxygen was close to unity. Certainly, the oxygen order could not be much larger than unity; if it were, equations 7 and 8 show that δ_2 would be negative and, thus, the effective mole fraction of oxygen in the flame would be greater than in the initial mixture. It is possible that the oxygen order is significantly less than unity. This would imply, on the basis that the overall order was 2·3, that the order with respect to hydrogen was at least twice as large as that for oxygen.

If it is assumed that δ_2 in equation 7 is negligibly small, then, for hydrogen flames the order with respect to oxygen is about 0·9. In that case, the value predicted for m, the order with respect to hydrogen, is about 1·4. This value was actually obtained in ref. 3 from measurement of the change of g as nitrogen was progressively replaced by hydrogen at constant mole fraction of oxygen for equivalence ratios greater than unity. It was hoped that in this procedure as well as in the other, flame temperature would remain nearly constant. However, it was observed that, in this case, flame temperatures increased by more than 60°K between $\phi = 1{\cdot}00$ and $\phi = 1{\cdot}59$. The effect of this temperature change was neglected. Recalculation of temperatures has shown that the increase was actually somewhat larger, about 90°K. Detailed examination of *Table 1* and *Figure 5* will show that this increase in flame temperature is closely related to the failure of the correlation of hydrogen flames with equivalence ratio for equivalence ratios greater than one. It should be pointed out, then, that the failure to correlate successfully flashback data for rich hydrogen–oxygen flames with change of flame temperature does not impair the validity of orders of reaction determined in ref. 3, since those values could have been obtained without use of data for rich flames.

A few points may be noted with regard to the values of n' found for hydrocarbon flames.

The expected order of reaction with respect to oxygen is about unity. That *n'* is significantly larger than unity both with nitrogen and with argon as diluents suggests that the effective equivalence ratio in the flame zone is significantly smaller than the initial equivalence ratio. This follows from equations 7 and 8. In this respect, the behaviour of hydrocarbon and hydrogen flames appear to be different. The fact that the value of *n'* obtained in ref. 3 for hydrogen flames was very close to unity indicated that initial and effective equivalence ratios were equal. For hydrocarbon–oxygen–nitrogen flames, on the other hand, if one assumes that the flame reaction is first order in oxygen, an initial equivalence ratio of, for example, 0·6 corresponds to an effective equivalence ratio of 0·42. This effective degree of depletion in the flame zone of the reactant in excess agrees well with that found by Weil and Ellington from measurement of methane–oxygen–nitrogen burning velocities (equations 11 of ref. 13).

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