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Burning Velocities of Butadiene-1,3 with Nitrogen-Oxygen and Helium-Oxygen Mixtures*

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Burning velocities of nitrogen-oxygen-butadiene-1,3 and helium-oxygen-butadiene-1,3 have been measured at atmospheric and reduced pressures. At atmospheric pressure the ratio of 3.7:1 for the maximum burning velocities was obtained for helium compared to nitrogen as the inert gas. Reduction of pressure caused an increase then a decrease in burning velocity for helium-oxygen-butadiene-1,3. The maximum value of the burning velocity occurred at 300 mm pressure. Calculations of the equilibrium concentrations of H, O, and OH for the gas mixtures used have been made. Assuming that the controlling factor in the burning velocity is the back-diffusion of H-atoms, good agreement between calculated and experimental burning velocity ratios is obtained.

INTRODUCTION

ACCORDING to Tanford's theory¹ of burning velocity, the substitution of helium for the nitrogen of air should increase the burning velocity because (1) a higher temperature will be attained with consequent increase in atom and radical concentrations, and (2) a higher diffusion coefficient will result. In addition the linear burning velocity should be increased by diminishing the pressure. A comparison of bunsen-type flames of butadiene-1,3 with ordinary air and with a corresponding helium-oxygen mixture has been made in this laboratory with the expected results.

In addition to the burning velocity measurements, the concentrations of the radicals H, O, and OH have been calculated from thermodynamic

data. These calculations have been made to show that back-diffusion of H-atoms from the flame front into unburned gas is the controlling factor in determining the burning velocity. This has previously been shown to be true for carbon monoxide-hydrogen mixtures¹ and is the basis of the burning velocity theory of Tanford.

EXPERIMENTAL METHOD

Gas mixtures were made up by means of flow meters and fed to a silica burner which was enclosed in a large mantle to exclude secondary air and to permit reduction of pressure.

Two cathetometers, one mounted for measuring vertical distances and one mounted for measuring horizontal distances, were used for measuring the dead space, flame cone height, and cone base diameter. A second "projection method" was used

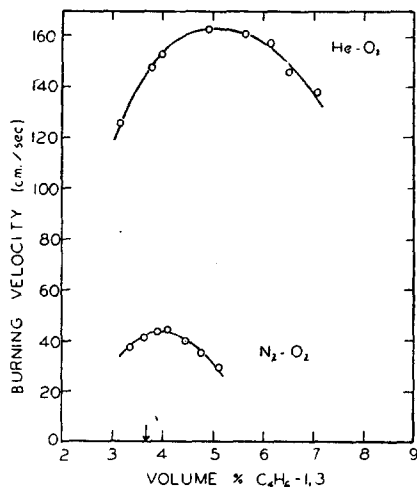


FIG. 1. Burning velocities of butadiene-1,3 (6.66-mm I.D. quartz mantled burner; atmospheric pressure).

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¹ C. Tanford and R. N. Pease, *J. Chem. Phys.* **15**, 431, 433, 861 (1947).

TABLE I. Burning velocities of nitrogen-oxygen-butadiene-1,3 and helium-oxygen-butadiene-1,3 at atmospheric pressure (6.66-mm I.D. quartz large mantled burner).

Oxidant rate (1/min.)*	C ₄ H ₆ -1,3 rate (1/min.)*	Vol. % C ₄ H ₆ -1,3	Flame base diam. (mm)	Flame height (mm)	Burning velocity (cm/sec.)
Helium-oxygen:					
12.9	0.35	2.86	lower limit		
	0.39	3.18	6.80	14.7	126
	0.47	3.81	6.70	12.8	148
	0.55	4.02	6.70	12.5	153
	0.62	4.95	6.70	11.7	163
	0.72	5.70	6.70	11.8	161
	0.78	6.16	6.70	12.3	157
	0.83	6.51	6.70	13.4	146
	0.91	7.10	6.80	14.8	138
	0.99	7.79	upper limit		
Nitrogen-oxygen					
4.00	0.121	2.93	lower limit		
	0.139	3.36	7.6	14.85	37.9
	0.151	3.64	7.4	13.80	41.9
	0.163	3.92	7.2	13.55	43.9
	0.171	4.10	7.2	13.50	44.3
	0.187	4.48	7.4	14.50	40.3
	0.200	4.76	7.6	16.15	35.4
	0.216	5.13	7.8	18.70	29.9
	0.277	5.38	upper limit		

* Rates at 25°, 760 mm pressure. Stoichiometric mixture—3.68 vol. % C₄H₆.

TABLE II. Burning velocities of butadiene-1,3 in nitrogen-oxygen and helium-oxygen at reduced pressures (10.55-mm quartz burner).

Flow rates*			Volume %	Cone areas (cm ²)			Burning velocities (cm/sec.)		
Pressure (mm Hg)	Oxi- dant	C ₄ H ₆ - 1,3		(1)**	(2)***	(3)†	(1)**	(2)***	(3)†
Helium-oxygen:									
180	14.0	0.40	2.79	2.09	1.43	1.98	115	168	121
180	14.0	0.61	4.16	1.67	1.49	1.54	146	163	158
180	14.0	0.74	5.04	1.97	1.63	2.02	125	151	122
180	14.0	0.83	5.62	2.67	2.41	2.87	92.6	102	86.1
300	14.0	0.39	2.69	1.72	1.64	1.65	139	146	146
300	14.0	0.47	3.28	1.32	1.48	1.50	183	163	161
300	14.0	0.60	4.09	1.35	1.51	1.44	180	161	169
300	14.0	0.73	4.92	1.97	1.85	1.56	125	133	157
450	14.0	0.36	2.50	1.95	1.89	2.11	123	127	115
450	14.0	0.41	2.85	1.63	1.63	1.68	147	147	142
450	14.0	0.86	5.76	2.12	2.06	2.10	117	120	118
450	14.0	0.96	6.41	3.15	2.92	3.04	79.1	85.4	81.9
Nitrogen-oxygen:									
300	14.0	0.50	3.43	4.34	4.38	4.11	55.7	55.0	58.8
300	14.0	0.54	3.68	4.31	4.07	4.23	56.2	59.7	57.3
300	14.0	0.66	4.47	5.15	5.06	5.09	47.4	48.3	48.0
450	14.0	0.53	3.63	4.88	4.98	5.04	49.6	48.6	48.2
450	14.0	0.61	4.19	6.79	4.80	4.92	50.8	53.7	

* All flow rates are given at the pressure indicated in liters per minute.

** The height and diameter at the base of the flame determined by cathetometer and the area determined by

$$A = \pi r(r^2 + h^2)^{1/2}$$

*** Dimensions determined by projection and area calculated as in (1).

† Dimensions determined by projection, area calculated by dividing the flame outline into frustums of cones and making a summation of the surface area using $\frac{1}{2}$ (sum of the perimeters) (slant height) to determine the area of each frustum.

for determining the flame dimensions. In this method, a light-tight box fitted with a transparent screen at the end was mounted directly behind the flame. An 80-mm diameter, 100-mm focus double convex lens was mounted in the box so that the flame was just outside the focus. In this way an inverted real image of the stationary flame was cast on the screen and traced on a thin piece of paper. A beam of light was used to obtain a projection of the burner tube of known outside dimension. By using an enlargement factor, it was possible to determine all the flame dimensions including the dead space. The method was essentially that used by Garsyth, Forsyth, and Townend.²

Three methods were used for determining the cone areas:

TABLE III. Calculated radical concentrations for butadiene-1,3 flames in helium-oxygen and nitrogen-oxygen (stoichiometric composition: 3.68 percent butadiene-1,3).

Inert gas	Total pressure (atm.)	Burning velocity (cm/sec.)	Calculated equilibrium flame temperature (°K)	Radical concentrations (atm.)		
				H	O	OH
N ₂	1	43	2380	0.00088	0.00086	0.0039
He	1	143	2660	0.00430	0.00470	0.0115
N ₂	$\frac{1}{2}$	53	2350	0.00057	0.00057	0.00233
He	$\frac{1}{2}$	179	2600	0.00264	0.00273	0.00600

² Garsyth, Forsyth, and Townend, The Institute of Fuel, p. 175 (1945).

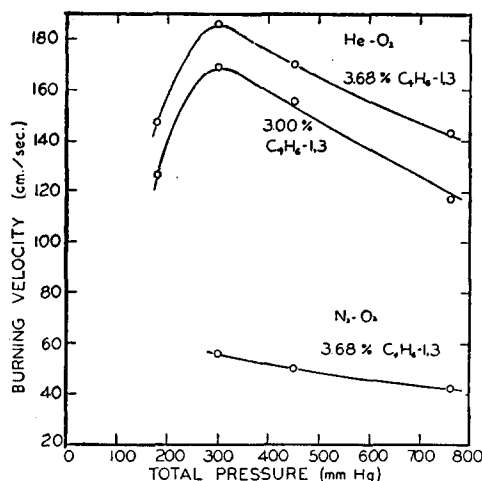


FIG. 2. Variation of burning velocity of butadiene-1,3 with pressure (cathetometer measurements; points at 760-mm, 6.66-mm burner; other values using 10.55-mm burner).

(1) Calculation using base diameter and flame height on the basis of an ideal cone from the cathetometer measurements.

(2) Calculation as in (1) with measurements taken from the projected image instead of the cathetometer measurements.

(3) Calculation from the projected image by obtaining the lateral areas of frustums into which the projected image was divided.

Burning velocities were calculated using the method of Gouy³ where

$$S = V/A$$

S = burning velocity in cm per sec.

V = volume feed rate of flow in cm³ per sec. at the operating pressure.

A = flame cone area in cm² calculated from $\pi r(r^2 + h^2)^{1/2}$.

Data for areas and burning velocities (V/A in cm per sec.) calculated by the above three methods are collected in Table II. In each case burning velocities were based on the outer cone areas. At the lower pressures the reaction zone appears to become thicker. If burning velocities had been based on the inner cone border or an intermediate border, somewhat larger burning velocities would have resulted.

TABLE IV. Comparison between experimental and calculated burning velocity ratios.

	He N ₂	expt.	He N ₂	calc.	1 atm. $\frac{1}{2}$ atm.	expt.	1 atm. $\frac{1}{2}$ atm.	calc.
Total pressure, 1 atm.		3.3		3.2		—		—
Total pressure, $\frac{1}{2}$ atm.		3.4		3.1		—		—
Inert gas, N ₂		—		—		0.81		0.88
Inert gas, He		—		—		0.80		0.90

³ Gouy, Ann. Chim. Phys. 18, 1 (1879).

To determine burning velocities at atmospheric pressure a 6.66-mm I.D. mantled (25-mm I.D. mantle) quartz burner was used.

Butadiene-1,3 was obtained from the Matheson Company. Helium-oxygen mixtures were obtained from the American Oxygen Company. By gas analyses the helium-oxygen mixture contained about 21 percent oxygen (analysis of several tank mixtures).

RESULTS AND DISCUSSION

In Table I and Fig. 1 data are shown for burning velocities of helium-oxygen-butadiene-1,3 and nitrogen-oxygen-butadiene-1,3 for a 6.66-mm burner. From these data it can be seen that the ratio of the maximum value for helium as compared with nitrogen is 3.7:1 corresponding to values of 163 and 44.3 cm/sec. There is, thus, a striking increase produced in the burning velocity when helium is substituted for nitrogen.

Data at reduced pressures (a 10.55-mm diameter burner was used so that lower pressures might be attained) are shown in Table II. The variation of burning velocity with pressure has been plotted (see Fig. 2) from values obtained from graphs of the data in Tables I and II for the composition 3.68 vol. percent and 3.00 percent butadiene-1,3. For helium-oxygen this correlation indicates an increase in burning velocity with decrease in pressure down to 300 mm. Below this pressure the burning velocity of helium-oxygen-butadiene-1,3 mixtures decreases.

Higher flame speeds in "helium air" have been observed in methane combustion by Coward and Jones.⁴ As they point out, the lower heat capacity of helium results in a higher flame temperature. This is borne out by the calculated values given Table III.

The concentrations of H, O, and OH have also been calculated from the thermodynamic data and are included in Table III. It will be noted that the increase in equilibrium H-atom concentration at either pressure on substituting helium for nitrogen roughly parallels the increase in burning velocity. Assuming that the controlling factor is the back-diffusion of H-atoms from the flame front into unburned gas, an approximate solution indicates that the burning velocities should be given by¹

$$u = A(c_0 D)^{\frac{1}{2}}$$

where A = a coefficient depending on mixture composition; c_0 = equilibrium H-atom concentration at flame temperature; and D = coefficient of diffusion for H-atoms into unburned gas. This equation is roughly obeyed (Table IV) when account is taken of the somewhat greater diffusibility into "helium air." The higher flame velocities at lower pressures follow from the increase in diffusion coefficients (greater mean free path).

⁴ Coward and Jones, *J. Am. Chem. Soc.* **49**, 386 (1927).