TABLE III

ANODIC OXIDATION OF THALLIUM IN LIQUID AMMONIA SOLUTIONS OF AMMONIUM BROMIDE

Molar concn. NH_4Br	Current density amp./sq. cm.	V_i	V_e	V_{ox}	Theoretical oxidizing power recovered, %
0.60	0.008	2.01	..	..	..
.70	.008	1.21	..	..	..
.70	.008	1.50	..	..	..
.35	.013	1.25	1.27	..	..
.35	.013	1.20	1.22	1.19	88.0
.60	.013	1.19	1.21	1.17	80.0

Qualitative tests on the anolyte showed the presence of both thallous and thallic ions.

A few salts other than ammonium bromide were also used as electrolytes, with the results shown below. The current density in each of these experiments was 0.012 amp. per sq. cm. The solutions remaining after electrolysis were tested for oxidizing power.

One fact is outstanding: when the electrolyte consists of a nitrate, the corrected mean valence number is always approximately 1. With the other two electrolytes, ammonium chloride and potassium amide, however, values considerably higher than 1 are obtained. The negative test for oxidizing power when ammonium chloride is used as electrolyte is inconsistent with the value obtained for the mean valence number; a possible explanation is that the thallium anode may be partially passive in this case.

TABLE IV

ANODIC OXIDATION OF THALLIUM IN LIQUID AMMONIA SOLUTIONS OF VARIOUS SALTS

Electrolyte and molar concn.	Temp., °C.	V_i	V_e	Qualitative test for oxidizing power
1.0 NH_4NO_3	−50	0.92	0.95	......
0.8 $NaNO_3$	−75	.98	.99	Negative
0.25 $Zn(NO_3)_2$	−75	.98	.99	Negative
0.1 $Zn(NO_3)_2$	−70	.97	.99	Negative
0.8 NH_4Cl	−75	1.34	1.38	Negative
Satd. soln. of KNH_2	−60	2.33	2.41	Positive

Acknowledgment.—The authors are indebted to the Research Corporation for a Frederick Gardner Cottrell grant which has made this investigation possible.

LAWRENCE, KANSAS RECEIVED APRIL 30, 1951

[CONTRIBUTION FROM THE DEFENSE RESEARCH LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Effect of Composition on Burning Velocities in Hydrogen–Bromine Mixtures[1]

BY STONE D. COOLEY, JAMES A. LASATER AND ROBBIN C. ANDERSON

Burning velocities (for flames in hydrogen–bromine mixtures) have been determined by using a Bunsen-type burner. The effects of the type of atmosphere, size of burner tube, position of burner, etc., have been investigated. The maximum burning velocity observed, for mixtures at 49° and atmospheric pressure was 32 cm./sec. at 41–44 mole % bromine. Absolute values of burning velocity depended somewhat upon experimental conditions, but the trend of variation with composition was not affected.

The reaction of hydrogen and bromine, $H_2 + Br_2 \rightarrow 2HBr$, offers interesting possibilities as a system for investigating and testing modern concepts of flame propagation. The work of Bodenstein, Christiansen, Polanyi and others[2] has shown that the reaction occurs by a chain mechanism which is simple compared to those occurring in ordinary combustion systems, particularly since chain-branching is not be be expected.

$$\begin{aligned} Br_2 &\rightleftarrows 2Br \\ Br + H_2 &\longrightarrow HBr + H \\ H + Br_2 &\longrightarrow HBr + Br \\ H + HBr &\longrightarrow H_2 + Br \end{aligned}$$

The heat of reaction is small but Ohmann,[3] Sagulin[4] and Kitagawa[5] showed that flames can be ignited in hydrogen–bromine mixtures. Earlier experiments in this laboratory[6] showed that such flames would propagate smoothly, though slowly, through straight tubes; and preliminary calculations of theoretical flame temperatures, etc,, indicated no essential differences in mechanism of reaction to be expected in the flames as contrasted to ordinary conditions. Recently Kokochashvili[7] has reported further work on ignition of hydrogen–bromine mixtures.

Furthermore, in view of the question of diffusion of active particles as a factor in flame propagation, the hydrogen–bromine system is of interest because it involves only two such particles and these should differ appreciably in properties.

Experimental measurements of properties of hydrogen–bromine flames are, therefore, being made, for comparison with theoretical calculations. This report deals with results of measurements of burning velocities of mixtures of various compositions made using a bunsen-type burner.

Apparatus.—The burner itself consists of a monel metal jacket approximately 3 inches in diameter and two feet

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(1) Based partly upon a paper presented at sixth Southwest Regional Meeting, American Chemical Society, San Antonio, Texas, December, 1950.

(2) See, for example, N. Semenoff, "Chemical Kinetics and Chain Reactions," Chap. VI, Oxford Press, 1934; R. N. Pease, "Equilibrium and Kinetics of Gas Reactions," p. 112, Princeton University Press, 1942, p. 112.

(3) H. Ohmann, *Ber.*, **53**, 1429 (1920).

(4) A. B. Sagulin, *Z. physik. Chem.*, **1B**, 275 (1928).

(5) T. Kitagawa, *Rev. Phys. Chem. Japan*, **12**, 135 (1928).

(6) H. R. Garrison, J. A. Lasater and R. C. Anderson, "Third Symposium on Combustion, Flame and Explosion Phenomena," Williams and Wilkins Co., Baltimore, Md., 1949, p. 155.

(7) V. I. Kokochashvili, *J. Phys. Chem.* (*U. S. S. R.*), **23**, 15, 21 (1949); **24**, 268 (1950); *cf. C. A.*, **44**, 6707 (1951).

long with a glass tube running up the center. The jacket is equipped with glass ports for observation of the flame. The burner is provided with a movable tungsten spark gap for igniting the mixtures. It is supported by trunions located at the mid-point of the jacket so that it can be inclined at any angle from vertical to horizontal.

A straight section was provided in the burner tube of at least forty tube diameters, so that pipe flow was fully developed. Since the Reynolds number for the mixtures as used ranged from 360 to 1900, the flow was essentially laminar.

Provision is made for inert gas to flow continuously through the burner to give an inert atmosphere for the flames. A heater and manometer are provided so that constant atmospheric conditions can be maintained.

The hydrogen flows from a cylinder through a glass capillary, differential-manometer type flowmeter.

Bromine vapor is supplied by a "bromine boiler" in which liquid bromine is vaporized in three horizontal glass tubes about 4 inches long and $^3/_4$ inch in diameter, filled with small glass rings. The tubes are wrapped with chromel wire, for heating. The rate of vaporization is controlled by a variable resistance in the electric power supply. Two 100-ml. glass bulbs connected in series, with capillary jets delivering into each bulb, are placed in the line between the boiler and the meter. The high pressure drop and turbulence in the bulbs effectively smooth out pressure fluctuations in the bromine vapor flow before it enters the metering device.

All connecting lines for bromine flow are of glass, jacketed with asbestos and heated electrically to avoid condensation.

In earlier measurements a glass capillary with a differential pressure manometer was used to meter the bromine flow. This type meter offered the advantages of great sensitivity and wide range, but condensation of bromine vapor caused serious difficulties. A special rotameter was then provided to meter the bromine. This rotameter is equipped with a lava or black glass float and Teflon float stops. To prevent condensation of the bromine vapor, the rotameter is enclosed in a glass jacket through which air at 100° is circulated.

Photographs of the hydrogen–bromine flames were taken with a Speed Graphic camera mounted on a tripod just in front of the glass port in the burner jacket.

Calibration.—The bromine rotameter and orifice flowmeter were calibrated under actual operating conditions by two different methods. The first method involved absorption in a potassium iodide solution of the bromine vapor flowing through the tube in a measured period of time. The second method involved freezing out the bromine vapor flowing through the tube in a measured time interval and weighing the solid bromine.

The hydrogen flowmeter was calibrated by collecting known volumes of the gas over water.

All measurements were carried out at atmospheric pressure. This pressure was 746 mm. on the average.

The temperature of the gas mixture emerging from the burner tube tip was measured with a copper–constantan thermocouple. The exact temperature of the mixture was a function of several variables including the total gas flow rate, the bromine rate, and hydrogen rate. The mean temperature of the gas mixture was found to be 49° with maximum variations of plus or minus 4°.

Calculations.—The volume of gas per unit time was calculated, using the perfect gas law, from the total moles of hydrogen and bromine as measured by the two flowmeters. Experimental data obtained earlier[8] indicate that at temperatures below 100°, the actual volume per mole of bromine is less than that for a perfect gas. However, the present experiments involve mixtures with relatively low percentages of bromine, and measurements of the densities of the hydrogen–bromine mixtures show no significant deviation from values calculated using the perfect gas laws.

For calculating the volume rate of gas issuing from the burner tip, 49° was used as the gas temperature. The use of this average temperature introduces a *maximum* possible error of 1.2%. The average linear velocity of the mixture emerging from the combustion tube was found by dividing the volume flow rate by the cross-sectional area of the tube. The composition was obtained from the readings of the hydrogen and bromine flowmeters.

Four enlarged tracings of each flame were made by projecting the negative photograph of the flame on sheets of graph paper. The angle of the flame cone was measured by drawing at about the mid-point of each side of the cone two tangents which corresponded most closely to the sides of the cone, the angle of intersection of these two tangents being considered as the angle of the cone. The average angle of the four tracings was used to calculate the burning velocity from the gas flow velocity.

For flames closely approximating cones [such as Fig. 1c], this method gives consistent results. The maximum deviation of the correction for the cone angle for such a flame was 4% of the average value. Similar measurements of the type of flame illustrated in Fig. 1b gave a maximum deviation from the average value of only 1%, while maximum deviation for the type flame in Fig. 1d was found to be 15%.

A much more laborious method, but one giving more consistent results for flames of somewhat distorted shape, was based upon determining the total surface of the flame and dividing this into the volume rate of gas flow through the flame. The surface area was determined from tracings of photographs of the flames by the method used by Hahnemann and Ehret.[9]

Materials.—The bromine was the reagent grade, J. T. Baker Analyzed, meeting the American Chemical Society standards. The hydrogen was oil pumped, electrolytic hydrogen. It had a 99.8% purity. Mixtures of hydrogen and each of three diluent gases were obtained commercially. The diluent gases were helium, argon and nitrogen. The helium used in these mixtures was of 99.2–99.8% purity with nitrogen as the chief impurity. The argon used was of 99.6% purity, and the nitrogen of 99.9% purity. Analysis made by density determinations gave percentages [by volume] of 20% of the diluent.

The gases used for atmosphere were nitrogen, carbon dioxide and helium. The nitrogen and helium were the same quality reagents as in the gas mixtures discussed above. The carbon dioxide was "bone dry" and had a 99.9% purity.

Results

Nature of Flames.—The general appearance of the flames was consistent with earlier results.[5,6] With minimum mole percentage of bromine in a mixture the "flame" appeared essentially as a line of demarcation at which the bromine color disappeared. As the percentage bromine was increased the yellow or orange color attributed by Kitagawa to excited bromine appeared with increasing intensity.

The shape of the flame varied very markedly with experimental conditions. Figure 1 shows a typical series of flame shapes. Mixtures of low bromine content commonly gave flames appearing as flat discs. These changed to hemispherical and conical shapes as the bromine content of the gas was increased. With 45 mole % bromine and above, elongated tips appeared on the cones. In some cases these tips appeared to be blown out, as indicated in the last flame illustrated. With the apparatus used here, the flame shape was fairly closely related to composition. Increased gas flow rates might change a flat flame, for example, to a very low cone, but quite commonly the flame would still be essentially a flat disc when the blow-off point was reached. A distorted-cone flame on the other hand, could not be pulled down flat by decreasing the gas flow-rate.

In general, above stoichiometric proportions of bromine, the flames flickered badly and were quite unstable. In some cases a "tip" 2–3 cm. high could be observed on a cone only about 1 cm. in height. Careful visual observations have indicated flame

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[8] James A. Lasater, Stone D. Cooley and Robbin C. Anderson, This Journal, **72**, 1845 (1950).

[9] H. Hahnemann and L. Ehret, *Z. Tech. Phy.*, Nr. 10–12, 1943, pp. 228–242 [*cf.* NACA Tech. Mem. 1271].

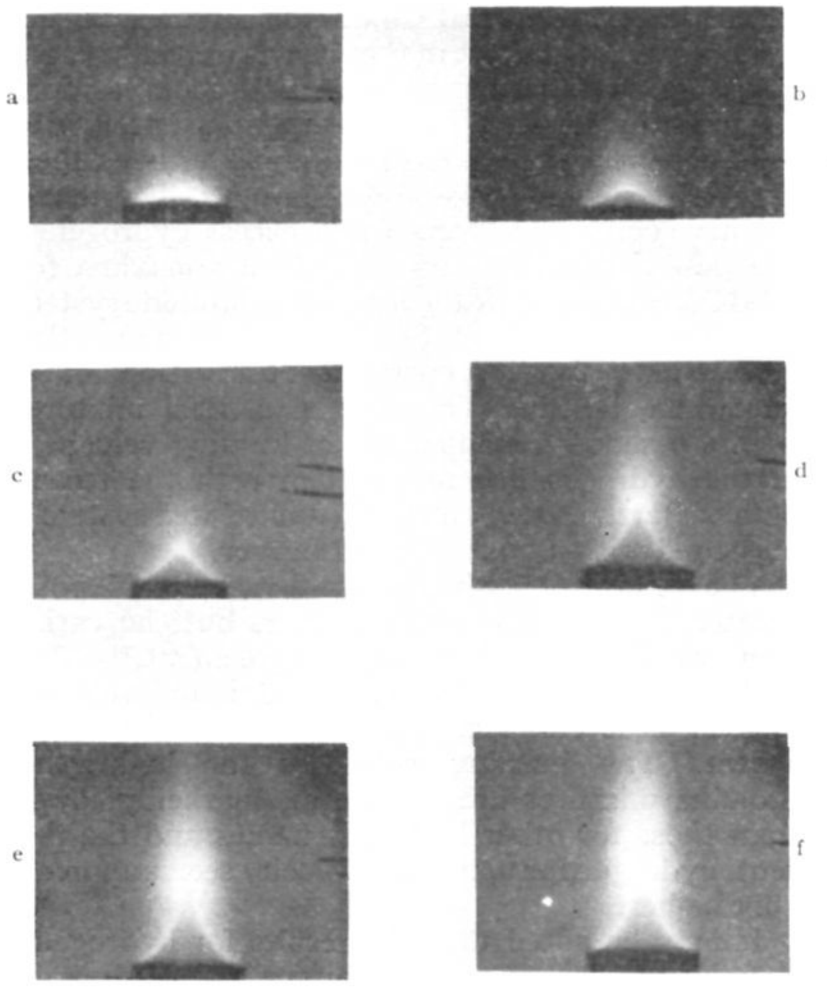

Fig. 1.—Flame photographs.

fronts for mixtures containing up to 60 mole % bromine, but even these may quite possibly not be continuous across the burner port. Ignition has been reported[7] for mixtures containing from 20% to as much as 98% bromine; but the tests in static tubes[6] showed that, with excess bromine, the flame commonly propagated through only a portion of the tube. It can however be clearly demonstrated that the burning velocity decreases markedly as the bromine content is increased above 45%. If for example a mixture containing 45% bromine is ignited and the hydrogen flow rate then decreased slowly, the per cent. bromine will be increased and the total gas flow rate decreased; yet the flame height increases markedly. At 50% the flame height is almost double that at 45%.

Effects of Experimental Conditions.—Figure 2 shows some typical measurements for two different burner positions. The points shown were chosen to illustrate the maximum range of variation in the observations. Figure 3 shows typical average results, using different flowmeters and atmospheres. (The small numbers indicate the number of independent measurements averaged for each point.) With helium as atmosphere, the observed burning velocities were somewhat higher than those shown. Figure 4 shows average data for a larger tube. Measurements were also made on tubes 0.57 cm. and 0.80 cm. in diameter. These were more difficult to work with but showed a trend of values consistent with those for the two larger tubes.

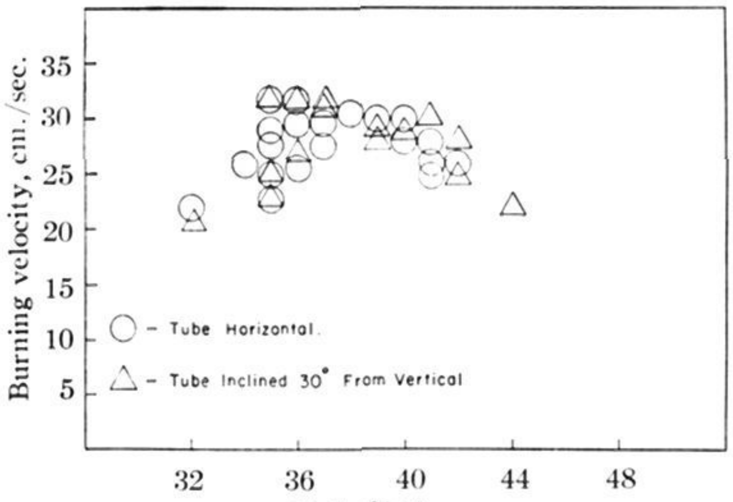

Fig. 2.—Burning velocities, 1-cm. tube, CO_2 atmos.

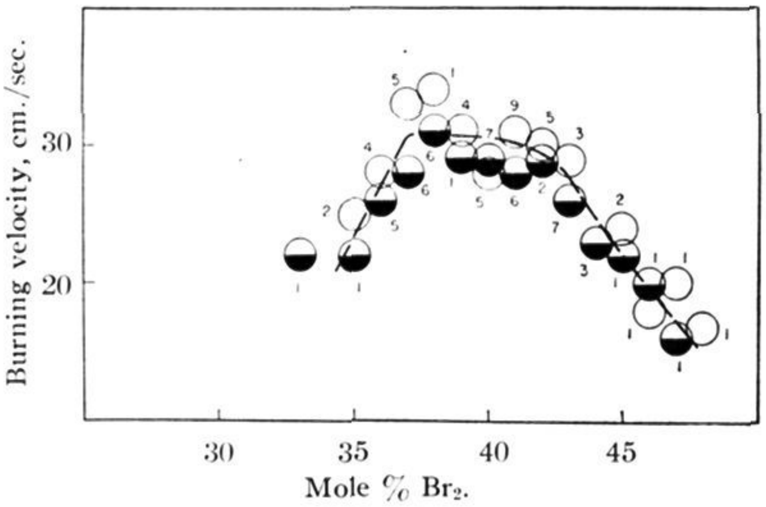

Fig. 3.—Burning velocities 1-cm. tube, vertical: O, orifice flowmeter, CO_2 atmosphere; ◒, rotameter, N_2 atmsophere.

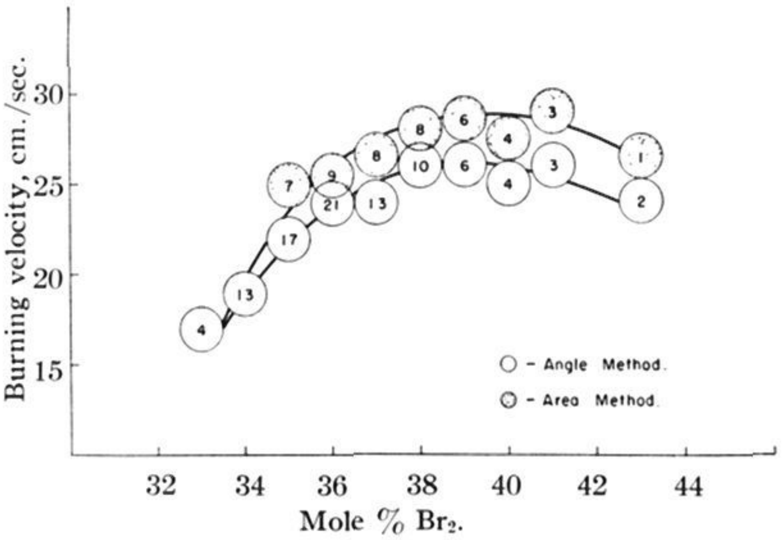

Fig. 4.—Burning velocities, 1.52-cm. tube, vertical.

The burning velocity was determined by the angle method for these comparative measurements because of its quickness. Figure 4 and Fig. 5 show a comparison of values determined by the

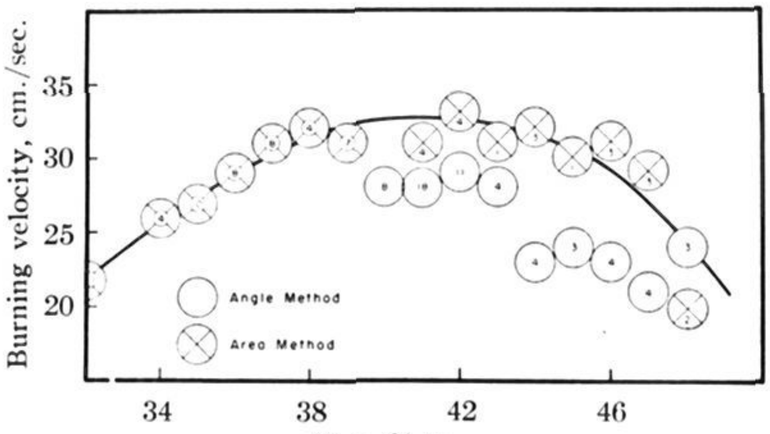

Fig. 5.—Burning velocities, 1.0-cm. tube, CO_2 atm.

angle method with those determined by the more laborious method using total flame area. Divergence is appreciable, of course, in the region where the flame shapes begin to be distorted, in which regions the area data should be more reliable.

No data are shown for mixtures with 50 mole % bromine or more. As noted above, such mixtures give flickering, unstable flames. Any data on these would be highly uncertain.

Effects of Other Gases.—Comparative tests of nitrogen, argon and helium as diluents were made by using tank mixtures of 80% hydrogen plus 20% diluent in place of pure hydrogen. For mixtures with excess bromine or a small excess of hydrogen, no observable effect was found. With lower percentages of bromine, the diluents decrease the burning velocity, the magnitude of the decrease being of the order of 50% for N_2, 35% for argon, and 15% for helium as diluent.

Small amounts of oxygen, water vapor, air, and hydrogen bromide were all found to decrease the burning velocity.

Discussion

Numerous analyses of burner data within recent years have emphasized the difficulties of obtaining absolute values of burning velocities. It is readily apparent that the numerical values of the burning velocities observed here are dependent to some extent on experimental conditions. However, the point of major interest in these measurements is the variation of burning velocity with composition. For this the results show a consistent pattern with different inert atmospheres, different burner tubes, and different positions of the burner. The maximum velocity clearly occurs in excess hydrogen—the best data so far available giving maxima for 42–44% bromine. If the hydrogen–bromine system be considered as a "fuel"—"air" system, this corresponds to the common observation of a maximum burning velocity in a rich mixture. Figure 6 shows a comparison of burning velocities in the hydrogen–bromine system with the recent data of Bartholome[10] on H_2–Cl_2 and related systems, measured with a nozzle-tipped burner.

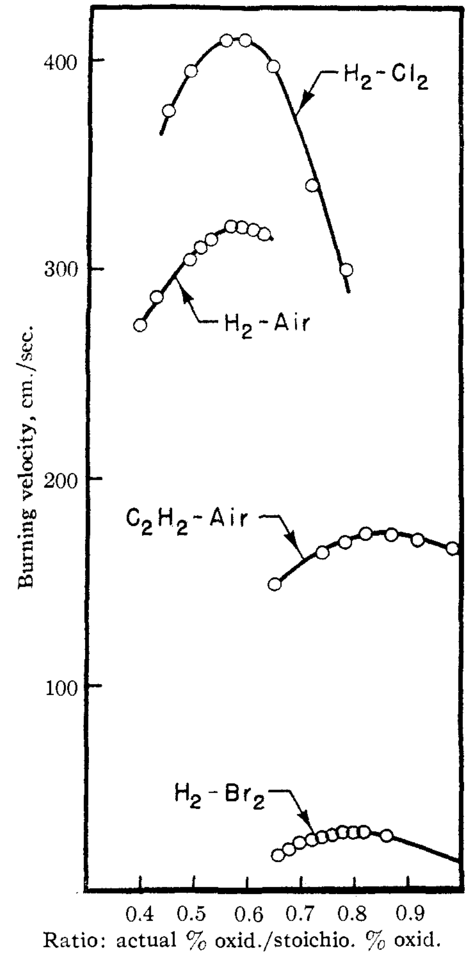

Fig. 6.—Burning velocities.

The values for hydrogen–air flames are 25–30% greater than those of other workers but the variation with composition is in agreement.[11] The hydrogen–oxygen system (with maximum velocity of over 1100 cm./sec.) could not conveniently be shown. The burning velocities for hydrogen–bromine mixtures are, of course, markedly lower than those for other hydrogen flames and the per cent. hydrogen for maximum velocity seems appreciably higher.

It may be noted that the results for hydrogen–bromine flames on larger burner tubes show a somewhat decreased burning velocity. This effect is not large and is not much beyond experimental error, so no conclusions are justifiable until additional data are available. The effect is being explored further, particularly at lower pressures. The change is in a direction contrary to that usually found, but a possibility that it is real lies in effects reported recently by Kokochashvili,[7] who concluded that appreciable dissociation of bromine was occurring on the walls. The effect does not, however, influence the variations of burning velocity with composition as observed.

It is also of interest to note that in this system, diffusion of hydrogen *into* the flame front from the approaching unburned gas may be appreciable. This offers a possible explanation for the rather strong tendency of flames on the low bromine side of the maximum to flatten out and those on the high bromine side to develop elongated tips.

The effect of composition on burning velocity is evidently not determined by temperature alone. Calculations of theoretical flame temperatures have already been made.[6] These show the maximum possible temperatures to occur in flames in mixtures close to stoichiometric proportions (48–50% bromine). The maximum burning velocity occurs at an appreciably lower per cent. bromine. The data of Bartholome on hydrogen and chlorine also show no correlation of maximum burning velocity with maximum equilibrium temperatures. Comparisons of the observed effects of composition with those predicted by various flame theories will therefore be of interest. Calculations of burning velocities in various mixtures are being made, using several theoretical equations, for such comparison.

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(10) E. Bartholome, *Z. Elektrochem.*, **53**, 191 (1949).

(11) *Cf.* F. A. Smith, *Chem. Revs.*, **21**, 389 (1937).

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AUSTIN, TEXAS RECEIVED JUNE 7, 1951

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

The Vapor Phase Association of Butyric and Heptanoic Acids

BY R. E. LUNDIN, F. E. HARRIS AND L. K. NASH

Data secured in an experimental study of the vapor densities of butyric and heptanoic acids are presented. These data indicate that the length and/or branching of the hydrocarbon substituent attached to the carboxyl group is without appreciable effect on the heats of dimerization of the paraffin acids. The presence of one or more higher polymers in the acid vapor is strongly indicated; and the experimental data are shown to be entirely consistent with the hypothesis that the predominant higher polymer is a trimeric species of substantial stability.

The results of a recent study[1] of the vapor phase association of the vapors of acetic and trimethylacetic acids have indicated that though the predominant polymeric form is the dimer, the acid vapors also contain substantial proportions of a stable trimeric species. The heat of dimerization of both acids was found to be close to −14 kcal., and in both cases the heat of trimerization was of the same order as (slightly greater than) $^3/_2$ the heat of dimerization. This suggests that the trimer bonds are of a character similar to those of the dimer. The further investigation here reported was designed: (a) to define more closely the influence on the dimerization process of the nature of the hydrocarbon substituent of the acid; and (b) to secure further evidence bearing on the trimerization postulate, which is diametrically opposed to the tetramer hypothesis advanced by Ritter and Simons.[2]

The former point is of interest because the heat of dimerization reported by Fenton and Garner[3] for *n*-heptanoic acid is but −7.8 kcal., little more than one-half the generally accepted corresponding value(s) for the lower carboxylic acids. Fenton and Garner suggest that the heats of dimerization of the paraffin acids must fall off markedly with increasing bulk of the hydrocarbon substituent. However, there is no indication of such a trend in the previously reported results for the lower paraffin acids and further work was considered desirable.

The small degree of polymerization of heptanoic acid vapor hinders the study of the dimerization, and effectively excludes the possibility of a meaningful examination of the trimerization process. It also appears[4] that heptanoic acid undergoes some decomposition at its boiling point. These circumstances suggested the desirability of limiting the work with heptanoic acid to a short series of measurements—made as rapidly and at as low temperatures as possible—while also making a more extended series of trials with a lower normal paraffin acid. *n*-Butyric acid was selected as the second subject of investigation.

Heptanoic Acid.—Heptanoic acid, twice vacuum distilled at room temperature, was found to melt at −8.7°. There is no agreement among the recently cited values for the melting point of this acid, the figures given ranging from −10.5 to −6.3°. A sample of the vacuum distilled heptanoic acid was introduced into the balance system[1] and a short series of measurements at minimum temperatures (and, necessarily, low pressures) was made as rapidly as possible. The results are given in Table I. The gas density, d, was determined from the balance readings, interpreted with the aid of check calibrations with carbon tetrachloride performed both before and after the trials with the acid. The values of M, the apparent molecular weight, were derived by making appropriate substitutions in the equation: $M = dRT/P$. The figures for $-\log K_2'$ were calculated from the following expression for K_2', the apparent dimerization constant

TABLE I

EXPERIMENTAL DATA AND APPARENT DIMERIZATION OBTAINED WITH BUTYRIC AND HEPATANOIC ACIDS

t (°C.)	P (mm.)	d(g./l.)	M	$-\log K_2'$
		Heptanoic acid		
227.1	277.9	1.189	133.5	4.015
200.6	256.8	1.186	136.5	3.682
218.2	198.6	0.858	132.4	3.897
189.4	244.9	1.1725	138.1	3.552
		Butyric acid		
195.5	717.5	2.479	100.99	3.553
172.7	634.4	2.468	108.17	3.220
183.2	676.4	2.484	104.50	3.381
195.2	664.7	2.280	100.20	3.556
183.0	624.2	2.272	103.55	3.384
172.7	588.7	2.267	107.05	3.227
195.3	592.6	2.007	98.95	3.568
172.8	527.9	2.001	105.42	3.239
163.4	497.6	2.003	109.61	3.066
195.7	506.2	1.690	97.59	3.573
173.0	452.8	1.685	103.55	3.245
163.0	427.1	1.686	107.36	3.077
153.7	402.6	1.687	111.54	2.911
184.8	395.5	1.360	98.21	3.432
163.1	353.2	1.360	104.79	3.088
153.0	331.4	1.356	108.74	2.919
142.8	299.7	1.311	113.45	2.723
152.8	262.1	1.044	105.84	2.919
141.4	242.7	1.041	110.90	2.712

$$K_2' = \frac{m(M - m)}{P(2m - M)^2} \qquad (1)$$

In this expression m is the molecular weight of the acid monomer.

A plot of $-\log K_2'$ against $1/T$ was linear, within the experimental error. The least-squares line fitted to the experimental points is represented by the equation

$$-\log K_2' = 9.807 - 2900/T$$

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(1) E. W. Johnson and L. K. Nash, THIS JOURNAL, **72**, 547 (1950).

(2) H. L. Ritter and J. H. Simons, *ibid.*, **67**, 757 (1945).

(3) T. M. Fenton and W. E. Garner, *J. Chem. Soc.*, 694 (1930).

(4) W. O. Pool and A. W. Ralston, *Ind. Eng. Chem.*, **34**, 1105 (1942).