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

Burning Velocities in Deuterium–Bromine and Hydrogen–Bromine Mixtures

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Burning velocities for deuterium–bromine and hydrogen–bromine mixtures have been determined from observations of flame velocities for flames in horizontal tubes. The observed values for the ratio of the burning velocity in hydrogen to that in deuterium were in the range 1.55–1.59. Calculated values from either the Tanford–Pease or Semenov–Frank-Kamenetsky equations were in agreement with the experimental observations, within the limits of accuracy of the calculations. The burning velocities for hydrogen–bromine mixture were somewhat less than, but in general agreement with, earlier values from burner measurements. The maximum burning velocity occurred for mixtures close to 43 mole % bromine.

Experimental measurements of burning velocities, using a Bunsen-type burner, have already been reported.[1] Comparative measurements have now been made of flame propagation in straight tubes with hydrogen–bromine and deuterium–bromine mixtures. These data are useful for comparisons with the earlier results and also with predictions based on various theories of the burning velocity.

Experimental

The flame studies with the deuterium were carried out in a static system because the amount of deuterium which could be secured precluded the use of a bunsen-burner type apparatus. This method for studying flames has been described by Coward and Hartwell.[2] In order to compare the burning velocities of the hydrogen–bromine and deuterium–bromine flames under identical conditions, both systems were studied in this static combustion tube.

The flame propagation apparatus consisted of a borosilicate glass tube 120 cm. long with an average inside diameter of 20.7 mm. Ground spherical joints were sealed on each end of the tube so that short end-pieces 10 cm. long fitted with stopcocks, spark-gap and necessary lines could be attached. The tube, except for the end pieces, was enclosed in a wooden jacket four inches square made with front and top of plexiglass. Nichrome heating wire strung along the inside of the jacket made it possible to keep the tube at a constant temperature. The end-pieces were also wrapped with heating wire and were thermally insulated by an outside wrapping of woven glass tape.

The end-piece which contained the ignition spark-gap was fitted with an additional spherical joint and cap so that when the cap was removed just before firing, the tube exhausted to the atmosphere through a short horizontal extension of 12 mm. inside diameter and 3 cm. length. The cap also served as a method of introducing the bromine into the system since an ampoule of bromine with a long thin neck could be inserted in the cap and broken by a slight twist. The ignition end-piece also was fitted with a stopcock through which hydrogen could be introduced into the tube.

The other end-piece contained two stopcocks; one led to a mercury manometer and the other to a vacuum pump.

To determine the spatial flame velocities the flame was photographed directly with a moving picture camera. In order to obtain a distance scale, a 40-cm. lucite scale with marks inscribed at each centimeter was placed directly above the tube and lighted by two small electric bulbs placed one at each end of the scale. An electric timer which could be read to the nearest $^1/_{100}$th of a second was placed beneath the tube. By taking moving pictures on which were recorded the flame, the distance scale, and the timer, it was possible to obtain an accurate value of the linear velocity of the flame. A movie camera with an f 1.9 lens and shutter speeds up to 64 frames per second was used with Eastman Super XX film.

To obtain larger pictures from which to measure the flame surface area a Zeiss 120 camera with an f 2.8 lens and a shutter speed of $^1/_{400}$th of a second was employed. The only film which was found satisfactory for the still pictures was the DuPont type 428, and it was necessary to sensitize this film by a preliminary exposure to mercury vapor in order to record an image of sufficient density.

Procedure.—A sealed ampoule of bromine was placed in the cap which closed the exhaust exit of the tube and the system was then evacuated and flushed with hydrogen several times. After being flushed out the tube was evacuated by a rotary oil pump and all stopcocks leading into the tube were closed. The neck of the ampoule was broken by carefully twisting the cap, and the bromine immediately vaporized and filled the tube. The temperature of the tube was maintained at 50°, after temperature equilibrium was established. Hydrogen was then introduced, to a total pressure such as to give the desired composition for that run.

The gas mixture was allowed to remain in the tube for two hours in order to ensure thorough mixing by diffusion. At the end of this time the total pressure was again checked. The tube was then opened to the atmosphere by removing the cap from the exhaust exit. The mixture was immediately ignited at the open end by spark-ignition and the flame photographed after it had proceeded halfway down the tube. Since the final pressure in the tube was always somewhat greater than atmospheric pressure no appreciable amount of air entered the tube upon the removal of the exhaust cap.

Two series of runs were made at compositions of 37, 40, 43, 46 and 50 mole per cent. bromine. In the first series moving pictures were taken of the flame, timer and scale so that the linear velocity of the flame might be determined. In the second series a much larger picture of the flame was made for use in determining the surface area of the flame.

The procedure for the deuterium flames was identical with that described above for the hydrogen flames with the exception that the initial flushing of the tube was done with hydrogen.

Vibratory Effects.—The first runs for the determination of burning velocity in the tube were carried out with hydrogen–bromine mixtures, and these preliminary tests showed marked vibratory effects. These were eliminated, as suggested by the work of Coward, *et al.*[2] When loose glass-wool plugs were inserted in both ends of the tube, slight effects were still observed in mixtures at the lower composition limit of 37 mole per cent. bromine, with which a barely audible hum could be detected. There was, however, no apparent visible disturbance of the flames and the effect was not observed with hydrogen–bromine mixtures of other compositions or with deuterium flames even at that composition. The moving pictures of the flames showed smooth propagation once the plugs were used.

Burning Velocities.—The spatial velocity of the flames was determined from the moving pictures on which were recorded the flame, a distance scale and a timer. Plots of distance *versus* time for individual runs gave straight lines, indicating that the spatial velocities of the flames had remained essentially constant during their travel down the tube. In order to make certain that no appreciable flow of the unburned mixture in front of the flame was included in the spatial velocity as measured, the pressure at the closed end of the tube was observed by means of a manometer during the run. This manometer showed an increase of no more than 2 mm. when the flame was ignited and this lasted until the flame was extinguished.

The burning velocity of the flame was calculated by the equation[3]

$$U_f = (U_0 - U_g)\frac{A_t}{A_f}$$

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[1] Stone D. Cooley, J. A. Lasater and R. C. Anderson, THIS JOURNAL, **74**, 739 (1952); Stone D. Cooley and R. C. Anderson, *Ind. Eng. Chem.*, **44**, 1402 (1952).

[2] H. F. Coward and F. J. Hartwell, *J. Chem. Soc.*, 2676 (1932).

[3] R. S. Levine and M. Gerstein, N.A.C.A. Research Memorandum, RME51J05 (1951).

where

U_f = fundamental flame velocity
U_0 = spatial flame velocity
U_g = gas velocity ahead of flame
A_t = cross-sectional area of combustion tube
A_f = flame surface area

Since no appreciable gas flow existed under the experimental conditions, the equation becomes

$$U_f = U_0 \frac{A_t}{A_f}$$

This, in effect, amounts to dividing the volume of gas burned per unit time by the area of the flame. The surface area of the flame was calculated from measurements taken from photographs by the method of Coward and Hartwell[2] as modified by Levine and Gerstein.[3]

Materials.—The bromine was the reagent grade, chemically pure, and met the American Chemical Society standards. The hydrogen was oil pumped, electrolytic hydrogen with a purity of 99.8% and was contained in a standard gas cylinder. The deuterium was obtained from the Stuart Oxygen Company of San Francisco. It had been dried with liquid air and was labeled greater than 99.5% pure.

Results

Burning velocities were measured for mixture compositions of 37, 40, 43, 46 and 50 mole per cent. bromine for both the hydrogen and deuterium flames. The initial temperature of all mixtures was 50° and the pressure was atmospheric, which varied from 738 to 760 mm. with most of the runs in the region of 746 mm. Table I shows the spatial velocity, ratio of tube area to flame area, and burning velocity for these mixtures, as well as the ratio of the burning velocity of hydrogen–bromine to deuterium–bromine flames at corresponding compositions.

The values for spatial velocities and for the ratios of the area of the tube to the flame area are average values. In the case of hydrogen flames they are averages of ten individual values, but for deuterium flames they are the averages of only four individual values. The area ratios for 37% mixtures are not as reliable as the ones at 40, 43 and 46% since the flames were dim and gave poor images. The area ratios in the 50% mixtures have no absolute significance since the flames became very elongated and combustion seemed to be occurring in a region of at least 20 cm. in the tube. There was no discrete boundary at the rear of the flame where burning ceased. These ratios are upper limits but they do show that at 50% the burning velocity has decreased markedly from the maximum value which occurs in the 40–43% region.

For the hydrogen–bromine mixtures, some tests were also made on flames propagating downward in a vertical tube. In the region of stable flames where burning velocities were determined, the results did not differ appreciably from those for the horizontal tube.

TABLE I

HYDROGEN–BROMINE AND DEUTERIUM–BROMINE BURNING VELOCITIES

	$H_2 - Br_2$			$D_2 - Br_2$			
Bromine, %	Spatial velocity, cm./sec.	$\frac{A_{tube}}{A_{flame}}$	Burning velocity, cm./sec.	Spatial velocity, cm./sec.	$\frac{A_{tube}}{A_{flame}}$	Burning velocity, cm./sec.	Ratio of vel. H_2/D_2
37	29	0.65	19	18.5	0.65	12	1.58
40	38	.61	23	23.8	.61	14.5	1.59
43	42	.57	24	27.4	.57	15.5	1.55
46	46.3	.49	22.5	29.7	.49	14.5	1.55
50	47.6	<.3	<14	33.6	<.3	<10	..

Discussion

The burning velocities obtained for hydrogen–bromine mixtures from the flame velocities in tubes are consistent with the earlier results with the bunsen-burner. In the burner experiments, the maximum burning velocity occurred in the general region of 40–44 mole per cent. bromine. In the tube experiments the maximum burning velocity was observed to occur specifically at close to 43% for both hydrogen and deuterium. This is in agreement with theoretical calculations.[4]

The burning velocities of hydrogen–bromine flames measured in the tube were somewhat lower than those measured by the bunsen-burner technique, but this dependence of burning velocity upon the method of measurement is consistent with effects often noted in measurements of flame properties since it is impossible to eliminate completely wall effects, etc., which are dependent on the design of the apparatus used.[5]

The results on hydrogen–bromine flames are in agreement with the available information on results of Kokochashvilii.[6] His experiments were made at different pressure ranges and tube sizes, and no attempt was made to correct for variations in flame shapes. The effects for various mixtures cannot, therefore, be compared directly, but in general the burning velocity values are quite close in magnitude to the results reported here.

Calculations have been made of the ratio to be expected of the burning velocity with deuterium to that with hydrogen. The equations of Tanford and Pease and of Semenov and Frank-Kamenetsky were used. Rate constants and concentrations for deuterium and bromine were calculated as previously described,[1] using the data of Bach, Bonhoeffer, and Moelwyn-Hughes,[7] with energies of activation, etc., corrected for differences in the zero-point energies for deuterium and hydrogen and their compounds. Either equation could give ratios in the range of 1.4–1.9, in agreement with the observed values within the uncertainty of the calculations.

It is of interest to note that these ratios do not in this case offer any basis for choice between the two equations. For the Semenov equation it was assumed in derivation that $D = \lambda/\rho_0 C_p$. In these systems, the diffusion of hydrogen and deuterium atoms predominates over the other atoms or molecules, so the specific ratio D_H/D_D is found to be very close to the general ratio $(\lambda/\rho_0 C_p)_{H_2-Br_2}/(\lambda/\rho_0 C_p)_{D_2-Br_2}$. Analysis of the rate expressions shows that both equations involve the same rate constants and concentrations.[1] Flame temperatures for the two systems are essentially the same; so the net difference in the ratios obtained from the two equations is the factor of the energies of ac-

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[4] R. C. Anderson, THIS JOURNAL, **77**, 232 (1955).

[5] *Cf.* M. F. Hoare and J. W. Linnett, *Trans. Faraday Soc.*, **49**, 1038 (1953).

[6] V. I. Kokochashvilii, *Zhur. Fiz. Khim.*, **25**, 444 (1951); *cf. C. A.*, **45**, 7856 (1951).

[7] E. Bach, K. E. Bonhoeffer and E. A. Moelwyn-Hughes, *Z. physik. Chem.*, **B27**, 71 (1934).

tivation: $(E_{H_2-D_2})^{1.5}/(E_{H_2-Br_2})^{1.5}$, which appears in the Semenov–Frank-Kamenetsky calculation. This ratio is, of course, close to unity (41,395/40,310). Any differences in the two equations are, therefore, well within the range of uncertainty in the calculations.

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AUSTIN, TEXAS

[CONTRIBUTION FROM THE MOUND LABORATORY,[1] MONSANTO CHEMICAL COMPANY]

Preparation of Actinium Metal[2]

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Quantities of actinium sufficient to permit preparation of the metal have not been available heretofore. Actinium metal has been prepared on the milligram scale by reduction of actinium fluoride with lithium vapor. A high-purity product was obtained with a yield of 95%. It resembles lanthanum metal both chemically and physically. The melting point of actinium metal was found to be 1050 ± 50°. The melting point of actinium metal shows both a horizontal and vertical relationship to the melting points of metals adjacent to it in the periodic table. It lies between that of radium and thorium and is about 200° higher than the melting point of lanthanum.

Introduction

Sufficient quantitites of actinium have not been isolated heretofore to permit preparation of the metal. Whereas radium occurs in uranium minerals to the extent of 1 part in 3,000,000 (parts of uranium), actinium occurs to the extent of only 1 part in 15,000,000,000. However, since the advent of nuclear reactors, it has been possible to produce actinium artificially in sizable quantities by neutron bombardment of radium according to the reactions[4]

$$Ra^{226}(n,\gamma)Ra^{227} \longrightarrow Ac^{227} + \beta$$

The actinium can then be separated chemically from the radium by the methods of Hagemann.[5]

Fried, Hagemann and Zachariasen,[6] studied the preparation and properties of some actinium compounds. These compounds were prepared in microgram quantities and were characterized by their X-ray diffraction patterns. The preparation of metallic actinium was not reported.

In the work described actinium metal was prepared on a milligram scale by the lithium reduction of actinium fluoride in vacuum, and a study of some of its chemical and physical properties was made.

Because actinium is a highly radioactive and biologically dangerous material, personnel shielding and remotely-controlled equipment were used. Most of the developmental work was carried out with lanthanum as a stand-in for actinium.

Discussion

Rare earth halides usually are used as starting material for the production of rare earth metals.[7] To reduce rare earth (or, more specifically, lanthanum) halides, a strong reducing agent is required. Thus, a survey of alkali and alkaline earth metals and their halides was made from the standpoint of both their chemical and physical properties.

The vapor pressures of the various metals and halides were obtained from Brewer's tables.[8] In the reaction

$$LaX_3 + 3M \longrightarrow 3MX + La$$

it is important that the reducing metal halide be more volatile than any of the other reactants or products. For example, it is noted that at higher temperatures the vapor pressure of lithium bromide is above that of lithium metal. If lanthanum bromide could be reduced by lithium vapor, the equilibrium would be shifted to favor the formation of lanthanum metal by volatilizing the lithium halide. On the other hand, the reduction of lanthanum fluoride by calcium would not be desirable, since calcium fluoride has a vapor pressure much less than that of calcium metal and approximately the same as that of lanthanum fluoride.

The tables of thermodynamic and physical properties of the metals and metallic halides collected by Brewer and co-workers[8] permit the calculation of equilibrium constants for a number of reduction processes. These constants are useful in a qualitative way in determining which processes might be feasible; however, it must be remembered that many of the values given in these tables are necessarily only estimates, although probably the best estimates available.

In Table I are collected the calculated equilibrium constants K at 1,000, 1,250 and 1,500°K. for a number of possible reduction reactions. Large

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(1) Mound Laboratory is operated by Monsanto Chemical Company for the United States Atomic Energy Commission under Contract Number AT-33-1-GEN-53.

(2) Abstracted from U. S. Atomic Energy Commission Report MLM-881, August 5, 1953.

(3) (a) Monsanto Chemical Company, Inorganic Chemicals Division, Everett Station, Boston 49, Mass.; (b) Monsanto Chemical Company, Research and Engineering Division, Dayton 7, Ohio.

(4) (a) S. Peterson, U. S. Atomic Energy Commission, MDDC-1501, July, 1946; (b) "National Nuclear Energy Series, IV-14b," McGraw–Hill Book Co., Inc., New York, N. Y., 1949, p. 1393.

(5) (a) F. Hagemann, THIS JOURNAL, **72**, 768 (1950); (b) F. Hagemann and H. C. Andrews, U. S. Atomic Energy Commission ANL-4215, Oct. 1948 (classified); (c) F. T. Hagemann, "National Nuclear Energy Series, IV-41a," McGraw–Hill Book Co., Inc., New York, N. Y., 1954, p. 27.

(6) S. Fried, F. Hagemann and W. H. Zachariasen, THIS JOURNAL, **72**, 771 (1950).

(7) A. H. Daane, U. S. Atomic Energy Commission AECD-3209, pp. 14–20, Dec., 1950.

(8) (a) L. Brewer, "National Nuclear Energy Series, IV-19B," McGraw–Hill Book Co., Inc., New York, N. Y., 1950, pp. 28–32, 193–207; (b) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, *ibid.*, pp. 103–116.