

In the same manner, it might be predicted that the effective chelate formed with citrate ion employs the one five-membered ring available. The problem of the relative stabilities of five- and six-membered chelate rings has been discussed by Martell and Calvin.¹² The present results are in accord with the conclusions described there.

The author wishes to express his appreciation to Professor G. T. Seaborg and Dr. K. Street, Jr., for guidance in this work.

(12) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 134.

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Effect of Diluents on Burning Velocities in Hydrogen-Bromine Mixtures

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In earlier reports, the results of measurements made by using a special Bunsen-type burner to determine the burning velocities of hydrogen-bromine mixtures for different compositions¹ and temperatures² have been summarized. Some measurements of the effects of diluents on flame velocities in tubes have also been reported.³

These experiments have been extended to determine, by the burner method, the effects of diluents such as nitrogen, argon and helium on the burning velocities.

Experimental

The materials, apparatus and procedure were essentially the same as described in the earlier reports,^{1,2} except that an additional gas line was provided so that an inert gas might be introduced into the burner along with the hydrogen.

The burning velocities were determined, as described before, from the gas flow velocities and the area of the flames.

Results

The colors of the flames and the ranges of shape observed were similar to those for hydrogen-bromine mixtures,¹ but not necessarily for corresponding bromine-hydrogen ratios. There was a distinct tendency toward greater relative stability for the bromine-rich mixtures in the presence of the diluents, though the total range of composition for stable flames was decreased. Shapes of flames in the region of 50 mole % bromine in the presence of diluents were, for example, comparable to those observed for 45-46% bromine in the absence of diluents. These effects on stability are illustrated in Table I, which shows the range between flash-back and blow-off for various proportions of nitrogen in the hydrogen.

The flames were, however, generally more difficult to work with in the presence of diluents, showing more tendency to flicker. It was not possible to

(1) S. D. Cooley, Jas. A. Lasater and R. C. Anderson, *THIS JOURNAL*, **74**, 739 (1952).

(2) S. D. Cooley and R. C. Anderson, *Ind. Eng. Chem.*, **44**, 1402 (1952).

(3) H. R. Garrison, J. A. Lasater and R. C. Anderson, "3rd Symposium on Combustion," Williams and Wilkins Co., Baltimore, 1949, p. 155.

Flash-back			Blow-off	
N ₂ /H ₂	H ₂ /Br ₂	Gas flow veloc., cm./sec.	H ₂ /Br ₂	Gas flow veloc., cm./sec.
0.053	1.40	39.8	1.66	44.1
.111	1.30	39.4	1.55	43.7
.177	1.20	38.8	1.42	42.8
.250	1.06	37.4	1.27	41.6

(Br₂ flow = 4.4 × 10⁻⁴ mole/sec.)

work with more than 25% diluent in the hydrogen. Figure 1 shows comparative data on burning velocities for an initial temperature of 50°. (It is apparent that the lines as drawn have no absolute significance. They are sketched in simply to call attention to the general trends of values.) Measurements were also made for initial temperatures of 200°. Under these conditions, the mixtures containing diluent all gave values well below those for hydrogen-bromine mixtures. For mixtures with 34 mole % bromine, for example, the burning velocity for a hydrogen-bromine mixture was 80 cm./sec. That for a mixture with helium replacing 25% of the hydrogen was 53 cm./sec. For argon and nitrogen the corresponding values were, respectively, 46 and 35 cm./sec.

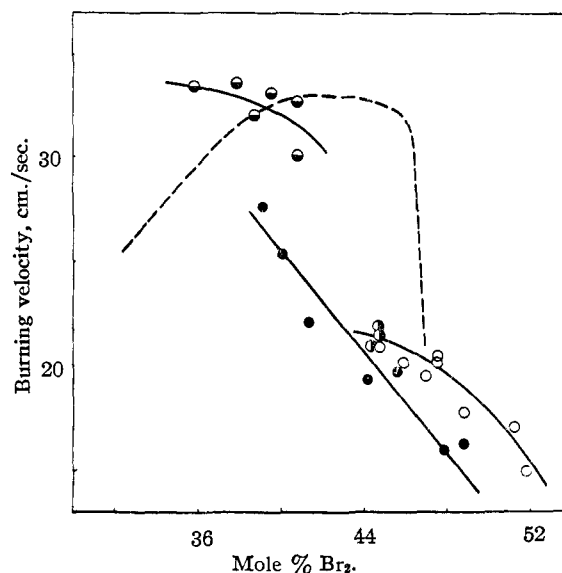


Fig. 1.—Effects of diluents at 50°: ---, no diluent; O, N₂/H₂ = 0.28; ●, N₂/H₂ = 0.33; ●, Ar/H₂ = 0.33; ●, He/H₂ = 0.33.

For mixtures of low bromine content, helium dilution tended consistently to increase the burning velocity, and with 11% helium in hydrogen, the burning velocities were higher for all mixtures tested. For 44 mole % bromine, for example, the burning velocity with helium added is around 34 cm./sec., whereas that for hydrogen alone plus bromine is down to about 20 cm./sec.

Discussion

In general, the effects of the diluents on burning velocities are consistent with the effects observed earlier on flame velocities in tubes.³ They also show the same trends and relative magnitudes as those reported by Wheatly and Linnett for acetyl-

ene-oxygen flames⁴ and by Clingman, Brokaw and Pease for methane-oxygen flames.⁵

For the hydrogen-bromine flames, the variations observed experimentally do not follow the patterns which might be expected on the basis of thermal or diffusion effects alone, *i.e.*, on the basis of variations in flame temperatures and heat conductances, or in diffusion coefficients. Such comparisons do not, of course, take into account kinetic effects on the reactions involved. Rabinowitch⁶ has, for example, found the order of effectiveness of these molecules in causing recombination of hydrogen and bromine atoms to be $N_2 > H_2 > A > He$, with helium and hydrogen being much less effective than the heavier molecules. Rice⁷ found the effective diameters for dissociation of molecular bromine to be $N_2 > A > H_2 > He$. The available data do not, however, permit any quantitative comparison between these and other factors.

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(4) P. V. Wheatly and J. W. Linnett, *Trans. Faraday Soc.*, **48**, 338 (1952).

(5) W. H. Clingman, R. S. Brokaw and R. N. Pease, "4th Symposium on Combustion," Williams and Wilkins Co., Baltimore, 1953, p. 310.

(6) E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 283 (1937).

(7) O. K. Rice, *J. Chem. Phys.*, **9**, 258 (1941).

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The Radical Sensitized Decomposition of Mixtures of Acetaldehyde and Formaldehyde¹

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In connection with an investigation of the thermal decomposition of formaldehyde initiated by radicals from ethylene oxide, it was of interest to compare the rates of the radical sensitized decompositions of acetaldehyde and formaldehyde when they are present together. Previous studies have shown that both acetaldehyde³ and formaldehyde⁴ can undergo induced decompositions in the presence of added substances yielding free radicals. Moreover, these aldehydes occur together as intermediates in certain thermal decompositions.⁵ Therefore, experiments were conducted with mixtures of acetaldehyde and formaldehyde with and without a sensitizer, such as ethylene oxide.

(1) The preliminary phases of this work were supported by the Office of Naval Research.

(2) E. I. du Pont de Nemours and Company Fellow, 1950-1951.

(3) A. O. Allen and D. V. Sickman, *THIS JOURNAL*, **56**, 2031 (1934); C. J. M. Fletcher and G. K. Rollefson, *ibid.*, **58**, 2135 (1936); A. Boyer, M. Niclaude and M. Letort, *J. chim. phys.*, **49**, 345 (1952).

(4) (a) S. Kodama and Y. Takezaki, *J. Chem. Soc., Japan, Pure Chem. Sect.*, **73**, 13 (1952); (b) unpublished results of James E. Longfield obtained in this Laboratory.

(5) (a) D. M. Newitt and M. A. Vernon, *Proc. Roy. Soc. (London)*, **A135**, 307 (1932); (b) W. Ure and J. T. Young, *J. Phys. Chem.*, **37**, 1169 (1933); (c) W. B. Gueither and W. D. Walters, *THIS JOURNAL*, **73**, 2127 (1951).

Experimental

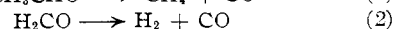
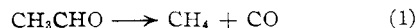
Formaldehyde was prepared from paraformaldehyde according to the method of Spence and Wild,⁶ and vapor pressure measurements over the range -74 to -18° were in agreement with their values (within the limits of experimental error $\pm 0.5^\circ$). The ethylene oxide was from the same supply and had the same rate of pyrolysis as reported earlier.⁷ The biacetyl from the Eastman Kodak Company was dried with anhydrous calcium sulfate and fractionated twice under vacuum. The acetaldehyde (Eastman) used in the preliminary experiments was fractionated under vacuum through a 70-cm. Vigreux column. The acetaldehyde samples from Eimer and Amend (Expts. 220-225) and Baker and Adamson (Expts. 241-247) were shaken for 30 minutes with sodium bicarbonate, dried over calcium sulfate and fractionated at atmospheric pressure through the above column with a partial condensation head.⁸ The material used in experiments 220-225 was a middle fraction with a boiling point of 19.8° at 745 mm. For experiments 244-245 the acetaldehyde was allowed to stand two hours at 0° over a small amount of hydroquinone and then distilled before use. All samples were carefully outgassed before introduction into the reaction vessel.

The reaction vessel was a 550-ml. cylindrical Pyrex bulb surrounded by three concentric aluminum tubes (6 mm. thick) and contained in an electrically heated furnace. The temperature at the center of the reaction bulb was measured with a platinum, platinum-13% rhodium thermocouple connected to a Leeds and Northrup Type K-2 potentiometer.

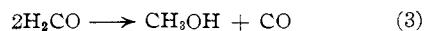
The initial analyses of the gaseous products removed at -196° were conducted by the mass spectrometric method.⁹ Since the mass spectrometric results indicated that only hydrogen, carbon monoxide and methane would be present in the non-condensable fraction, a method of gas analysis involving the oxidation of hydrogen and carbon monoxide over heated copper oxide was used. The unoxidized portion of the gas sample was considered to be methane. Tests with known mixtures showed essentially quantitative separation of the non-condensable gases ($\pm 0.5\%$) and satisfactorily correct percentages of the components ($\pm 0.5\%$).

Results

Table I shows the results of the analyses of the non-condensable gases present after mixtures of acetaldehyde and formaldehyde have been decomposed to the extent of about 30%. Inspection of the data reveals that the amount of pressure increase during a reaction is very nearly equal to the sum of the pressures of hydrogen and methane formed, while ordinarily the carbon monoxide is slightly larger than this sum. As in the case of the thermal decompositions of acetaldehyde³ and formaldehyde^{4b} investigated separately, the data are in agreement with the following reactions as the principal over-all processes



along with a lesser amount of the reaction



Reaction 3 has been found to occur with pure formaldehyde alone and the addition of 2 mm. of ethylene oxide at 415° does not appear to increase its rate more than 50%.^{4b} The chain lengths for reactions 1 and 2 are moderately long so that the ratio of methane to hydrogen can be used as a

(6) R. Spence and W. Wild, *J. Chem. Soc.*, 338 (1935).

(7) K. H. Mueller and W. D. Walters, *THIS JOURNAL*, **73**, 1458 (1951).

(8) The rates of pyrolysis upon comparison with values tabulated by J. C. Morris, *ibid.*, **66**, 584 (1944), agreed satisfactorily with the data of J. C. Morris and those of R. E. Smith and were slightly higher than the results of M. Letort.

(9) Analyses by Dr. F. L. Mohler and the staff of the National Bureau of Standards.