An Analysis of the Stability of Carbon Monoxide–Hydrocarbon–Air Flames[1]

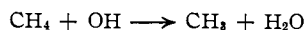BY ARTHUR LEVY AND PHILIP F. KURZ

RECEIVED JANUARY 13, 1954

Combustion studies with mixed fuels have shown that the stability limit of a mixture of two fuels normally falls between the limits of the individual fuels. An interesting anomaly occurs with carbon monoxide–hydrocarbon flames burning in air, in that this binary fuel mixture has greater stability than either the carbon monoxide or the hydrocarbon burning alone in air. Other research has shown that the slow, preflame oxidation of methane inhibits the oxidation of carbon monoxide. Consequently, carbon monoxide–hydrocarbon mixtures, before entering the flame zone, may be transformed to carbon monoxide–water vapor mixtures by preflame preferential oxidation of the hydrocarbon. The stabilities of the carbon monoxide–hydrocarbon flames reported by Walker and Wright agree with experimentally measured stabilities of carbon monoxide–water vapor mixtures of equivalent composition. Thus the apparent anomaly may be resolved, and the postulate of preflame preferential oxidation of the hydrocarbon in the mixture is supported.

Studies of the combustion of mixed fuels show that many fuels are compatible in the burning process, *i.e.*, they do not interfere with each other. There are, also, a number of instances in which one component of a binary fuel mixture inhibits the combustion reactions of the other fuel component. For example, hydrocarbons inhibit the explosion[2,3] and the flame propagation[4] of hydrogen in hydrogen–hydrocarbon mixtures, causing in the latter case large deviations from the LeChatelier rule for predicting rich-limit mixtures. Under conditions of either compatibility or inhibition, binary fuel mixtures burning in air have been found to have narrower stability limits than those of the faster burning component.

Walker and Wright[5] have recently reported studies of the flame stability of hydrocarbon–carbon monoxide fuel mixtures burning in air, which are of special interest because their results show that there are certain CH_4–CO–air and C_3H_8–CO–air mixtures which are more stable than the fastest burning, moist CO flames which they studied.

This paper uses results from kinetic studies of methane–oxygen reactions to explain the apparent anomalies in their results. The first part deals with the kinetics of methane and carbon monoxide oxidation; it is shown that the inhibiting effect of methane on the oxidation of carbon monoxide favors the conversion of CH_4–CO mixtures to CO–H_2O mixtures in slow or preflame reactions. In the second part, these results are applied to the flame stability data of Walker and Wright.

The Kinetics of Slow Reactions of Methane and Oxygen. Stepwise Oxidation of Methane.—The kinetics of methane oxidation are closely related to the kinetics of CO oxidation, inasmuch as the first steps in the oxidation of methane lead to the formation of only CO and water vapor. Present knowledge does not permit a complete understanding of the kinetics of the reactions involved; however, the basic steps for the high temperature oxidation of moist CO and of methane are outlined below.

Methane:

$$CH_4 + OH \longrightarrow CH_3 + H_2O$$

$$CH_3 + O_2 \longrightarrow HCHO + OH$$
$$HCHO + OH \longrightarrow CHO + H_2O$$
$$CHO + O_2 \longrightarrow CO + OH + H_2O$$

Carbon Monoxide:

$$CO + OH \longrightarrow CO_2 + H$$
$$H + O_2 + M \longrightarrow HO_2 + M$$
$$CO + HO_2 \longrightarrow CO_2 + OH$$

The mechanism of methane oxidation is clarified by the work of Garner and Ham[6] who studied the homogeneous flame reaction between methane and oxygen at 750°. They found that the reaction proceeds in four definite stages, which are: 1, preacceleration; 2, acceleration with increase in pressure; 3, reaction with decrease in pressure, which produces a flame; and 4, postflame reactions.

In the first stage, chain-propagating radicals are generated, and only small amounts of CO and H_2O are formed. In the acceleration stage larger quantities of CO, some CO_2 and H_2O are formed. Since CO is formed much faster than CO_2, the ratio CO/CO_2 is large. Most of the CO is oxidized in the flame reaction of the third stage. The small extent of the oxidation of CO to CO_2 in the slow, preflame reactions indicates that methane inhibits the oxidation of CO in this stage of the process.

Vanpee[7] made similar observations of the slow reaction of methane and oxygen at 400° and found that the reaction proceeds stepwise. In the first step CO and H_2O are formed, and in the second step CO is oxidized to CO_2. Both steps were found to be accelerated by water vapor. The rate equations were established as

$$r_1 = k_1(CH_4)^{2.3}(O_2)^{0.4}(H_2O)$$
$$r_2 = k_2(CH_4)^{1.3}(CO)(O_2)^{0.4}(H_2O)$$

Accelerating Effects of Water Vapor.—The accelerating effect of water vapor on the oxidation of CO is well established.[8] It has likewise been shown that water vapor accelerates the rate of combustion of hydrogen[9] and of ethane.[10] Accordingly it is reasonable to expect that water vapor accelerates the slow oxidation of all hydrocarbons in preflame reactions. It has been found
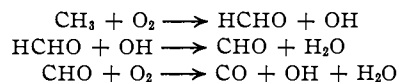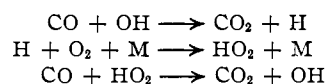
(1) Presented before the Gas and Fuel Division at the 124th meeting of the American Chemical Society, Chicago, Illinois, September 1953.

(2) (a) A. Levy, Battelle Memorial Institute Technical Report No. 15036-6 to Wright Air Development Center, Contract No. AF 33-(038)-12656, E. O. No. 460-35 S.R.-8, July, 1952, 24 pages.

(3) R. R. Baldwin, *Fuel*, **31**, 312 (1952).

(4) A. Levy, *J. Chem. Phys.*, **21**, 2132 (1953).

(5) P. L. Walker and C. C. Wright, *Fuel*, **31**, 37, 45 (1952).

(6) W. E. Garner and A. J. Ham, *Proc. Roy. Soc. (London)*, **A170**, 80 (1939).

(7) M. Vanpee, *Ann. Belg.*, **47**, 111 (1947-1948).

(8) G. Hadman, H. W. Thompson and C. N. Hinshelwood, *Proc. Roy Soc. (London)*, **A137**, 87 (1932).

(9) B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1951, Chapter 2.

(10) N. Chirkov, *Doklady Akad. Nauk. USSR*, **45**, 244 (1944).

further that methane accelerates the slow oxidation of hydrogen.[3] The accelerated reaction in methane–hydrogen mixtures has been shown to be due to the formation of water vapor in the slow reaction, which is quite analogous to the mechanism proposed here in explaining the $CO-CH_4$ reactions. Consequently the effects of hydrocarbons in slow oxidation reactions and in fast flame reactions are related to the water vapor effect. The small quantities of water vapor produced in the slow reactions accelerate the reaction rate, but the exceedingly large quantities produced in the flame reactions reduce the propagation rate.

Inhibiting Effect of Methane.—Figure 1, reproduced from Hirsch's studies,[11] illustrates the effectiveness of methane in inhibiting the oxidation of carbon monoxide. Hirsch passed a 1% mixture of methane in air through a heated combustion chamber with a residence time of 4 to 5 milliseconds. The methane was completely reacted only when the chamber temperature was 1020° or higher, and the major portion of the product, CO, reacted to form CO_2 only after the methane was almost completely consumed.
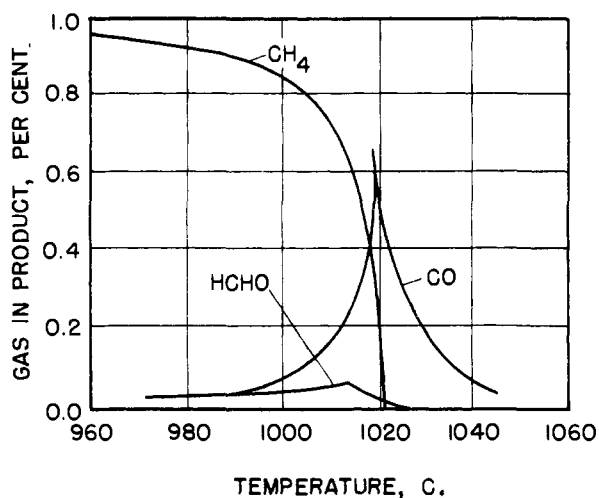

Fig. 1.—Methane combustion at constant residence time (ref. 11).

The Combustion of Carbon Monoxide.—It has been shown by several investigators that CO and oxygen in proportions of about 4.1:1 form the most stable or rapid burning mixture, and that the addition of about 6% water vapor to such a mixture further accelerates the reaction to its maximum rate.

Table I, taken from Bone,[12] illustrates this strong accelerating influence of water vapor on the flame speed of the most reactive CO–air mixtures, in which $CO/O_2 \cong 4.1$.

TABLE I

FLAME VELOCITY OF A MIXTURE OF 45% CO IN AIR, WITH VARYING WATER CONTENTS

H_2O, %	0.70	1.45	3.50	5.20	8.00
Flame velocity, cm./sec.	56	76	106	120	118

(11) See A. Egerton, *Fuel*, **31**, 385 (1952).

(12) See W. Jost, "Explosion and Combustion Processes in Gases," McGraw-Hill Book Co., New York, N. Y., 1946, p. 121.

The Stability of CH_4–CO–Air and C_3H_8–CO–Air Flames.—Walker and Wright have measured flashback limits for various mixtures of $CO-CH_4$ and $CO-C_3H_8$ over a range of fuel–air ratios for each fuel mixture. If it is assumed on the basis of the kinetic data cited in the preceding sections that the preflame reactions occur stepwise, with the hydrocarbon first being oxidized to CO and water vapor, then it is possible to calculate the composition of the gases entering the flame. For example, a mixture of 1 part CH_4, 10 parts CO and 30 parts air (or 6 parts O_2 and 24 parts N_2) would be converted by preflame oxidation of the methane to 11 parts CO, 2 parts H_2O, 4.5 parts O_2 and 24 parts N_2.

Table II shows the percentage composition of the saturated fuel–air mixture at maximum stability for each fuel composition studied by Walker and Wright. For the fuels containing 10% or less methane, the CO/O_2 ratio produced by the assumed preflame oxidation of CH_4 falls close to the value of 4.1 found for maximum stability in other experiments with CO flames. Furthermore, the fuel containing 7.5% methane produces the most stable flame of any of the fuel compositions at their respective points of maximum stability. The water vapor content of this mixture, calculated with the assumption of preoxidation of the methane, falls in the range of 5 to 8% as would be predicted from the data of Bone in Table I.

Tables III and IV show similar calculations for measurements on dry CH_4–CO and dry C_3H_8–CO mixtures burning in air. The same comments and deductions apply.

Other workers have also reported that hydrogen, as well as organic compounds containing hydrogen, accelerate the combustion of CO. For example, the addition of 1% hexane was found to increase the burning velocity of CO–air mixtures by 29.5%.[13] This large increase in flame speed by the addition of so small an amount of hexane is understandable if calculations similar to those performed on the CH_4–CO mixtures are made with the following two mixtures

$$31CO + 69air \qquad (1)$$
$$30CO + 1C_6H_{14} + 69air \qquad (2)$$
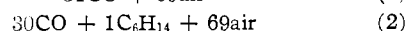
Mixture 1 consists of 31 parts CO, 13.8 O_2 and 55.2 parts N_2; and mixture 2, after preflame oxidation, is 36 parts CO, 7.8 parts O_2, 6 parts H_2O and 55.2 parts N_2. It is reasonable to expect that mixture 2 would burn faster than mixture 1 because it contains approximately 6% water vapor whereas mixture 1 does not. Furthermore it is probable that mixture 2 represents a mixture very near maximum stability for the $CO-C_6H_{14}$ system, since its CO/O_2 ratio equals 4.6.

It therefore appears that these anomalous flame stability results are not only explainable in terms of the slow, preflame reactions, but that they also serve to substantiate further the inhibiting effect of methane on the oxidation of carbon monoxide. It is not possible to explain from these studies the exact mechanism by which this interaction between methane and carbon monoxide occurs in these flames.

(13) K. Bunte and E. Hartman, Ph.D. Dissertation, Karlsruhe, 1931, p. 17.

TABLE II

COMPOSITION OF SATURATED CH_4-CO-AIR MIXTURES AT POINT OF MAXIMUM FLAME STABILITY

Fuel compn., % CH₄	CO	Velocity gradient at max. stability, sec.⁻¹	Fuel in fuel-air mixture, %	Initial compn. of combustible mixture, % CH₄	CO	O₂	N₂	Equiv. compn. after preflame oxidation of CH₄, parts CO	O₂	H₂O[a]	N₂	Ratio, CO/O₂
100	0	320	10	10	0	18	72	10	3	23	72	3.3
60	40	470	14	8.4	5.6	17.2	68.8	14	4.6	19.8	68.8	3.04
20	80	960	24	4.8	19.2	15.2	60.8	24	8.0	12.6	60.8	3.0
10	90	1300	34	3.4	31.6	13.2	52.8	34	8.1	9.8	52.8	4.2
7.5	92.5	1500	36	2.7	33.3	12.8	51.2	36	8.7	8.4	51.2	4.14
5	95	1400	40	2.0	38.0	12.0	48.0	40	9.0	7.0	48.0	4.44
2.5	97.5	1200	43	1.1	41.9	11.4	45.6	43	9.8	5.2	45.6	4.38
0	100	1000	45	0	45	11	44	45	11	3.0	44	4.09

[a] Includes water vapor carried by the saturated air.

TABLE III

COMPOSITION OF DRY CH_4-CO-AIR MIXTURES AT POINT OF MAXIMUM STABILITY

Fuel compn., % CH₄	CO	Velocity gradient at max. stability, sec.⁻¹	Fuel in fuel-air mixture, %	Initial compn. of combustible mixture, % CH₄	CO	O₂	N₂	Equiv. compn. after preflame oxidation of CH₄, parts CO	O₂	H₂O	N₂	Ratio, CO/O₂
100	0	430	9.5	9.5	0	18.1	72.4	9.5	3.8	19.0	72.4	2.5
60	40	630	14	8.4	5.6	17.2	68.8	14	4.6	16.8	68.8	3.04
20	80	1200	25	5.0	20.	15.0	25	25	7.5	10.	60.	3.34
10	90	1500	34	3.4	30.6	13.2	52.8	34	8.1	6.8	52.8	4.2
7.5	92.5	1500	37	2.8	34.2	12.6	50.4	37	8.4	5.6	50.4	4.4
5.0	95	1300	40	2.0	38.0	12.0	48.0	40	9.0	4.0	48.	4.44
2.5	97.5	1200	45	1.1	43.9	11.	44	45	9.4	2.2	44.	4.78
0	100	390	47	0	47	10.6	42.4	47	10.6	0	42.2	4.43

TABLE IV

COMPOSITION OF DRY C_3H_8-CO-AIR MIXTURES AT POINT OF MAXIMUM FLAME STABILITY

Fuel compn., % C₃H₈	CO	Velocity gradient at max. stability, sec.⁻¹	Fuel in fuel-air mixture, %	Initial compn. of combustible mixture, % CO	C₃H₈	O₂	N₂	Equiv. compn. after preflame oxidation of CH₄ parts CO	O₂	H₂O	N₂	Ratio, CO/O₂
100	0	600	4	0	4	19.2	76.8	12	5.2	16	76.8	2.31
40	60	730	10	6.0	4	18.0	72.0	18	4.0	16	72.0	4.5
10	90	1100	23	20.7	2.3	15.4	61.6	27.6	7.3	9.2	61.6	3.78
5	95	1300	34	32.6	1.4	13.2	52.8	36.8	8.3	5.6	52.8	4.43
2.5	97.5	1200	39	38.	1.	12.2	48.8	41.	8.7	4.	48.8	4.71
0	100	400	45	45	0	11	44	45	11	0	44	4.09

As was shown earlier, however, the basic steps in the oxidation of methane and of carbon monoxide are quite similar. It is probable that two of the main competing reactions are the reactions with the hydroxyl radical: $CH_4 + OH = CH_3 + H_2O$, and $CO + OH = CO_2 + H$. From the several examples shown in the first section it appears that the methane step takes precedence over the CO step. It is probable then that an important step in the CO mechanism is one which occurs before the above step, namely

$$CO + H_2O \xrightarrow{\text{surface}} CO_2 + H_2$$
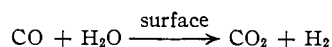
In such a case, the inhibition interactions may be explained by the fact that the surface reaction step is rate controlling for the carbon monoxide until sufficient water vapor is formed by the methane reaction to accelerate the CO oxidation. Then, since moist CO also follows the mechanism for the oxida-

tion of hydrogen and oxygen quite closely, the CO chains are probably propagated by the reactions

$$CO + OH = CO_2 + H$$
$$CO + HO_2 = CO_2 + OH$$
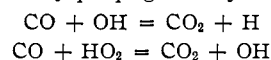
Summary.—Evidence from kinetic studies of the CH_4-O_2 reaction shows that methane inhibits the oxidation of CO in slow reactions. These facts have been used to explain the anomalous flame stability data obtained with CH_4-CO and C_3H_8-CO mixtures by considering that the hydrocarbon-CO-air mixtures are changed to mixtures of CO + H_2O + O_2 + N_2 before the flame reaction.

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