19. *The Rates of Detonation in Carbon Monoxide–Oxygen Mixtures.*

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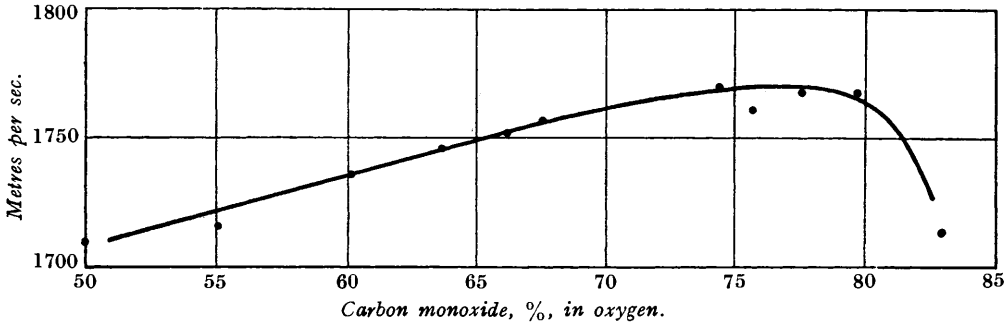
VARIOUS methods have been used to initiate detonation in gaseous mixtures. The simplest is that used originally by Berthelot and Vieille (*Compt. rend.*, 1882, **94**, 101), in which the mixture is ignited by an electric spark at one end of a long tube. When the mixtures

are fired in this manner, the length of run of flame before detonation is established depends upon the composition of the gas mixture and may be inconveniently great, as, *e.g.*, with mixtures of carbon monoxide and oxygen. In order to shorten this length, Payman (*Proc. Roy. Soc.*, 1928, **120**, *A*, 90) and Bone and Fraser (*Phil. Trans.*, 1931, **230**, *A*, 363) have used explosive " detonators "; with hydrogen–oxygen and methane–oxygen mixtures detonation is thereby set up almost immediately. For the same purpose Bone and Fraser (*Proc. Roy. Soc.*, 1931, **130**, *A*, 542) have used a " detonating box " consisting of a labyrinth of baffle plates inside a metal chamber.

Detonation can also be fairly readily established in a carbon monoxide–oxygen mixture by introducing around the spark gap, before ignition, a small amount of electrolytic gas or similar mixture (cf. Dixon, *Phil. Trans.*, 1893, **184**, *A*, 171). This method has been adopted in the present experiments, which were designed for the measurement of the rates of detonation in carbon monoxide–oxygen mixtures, with the mixtures $2H_2 + O_2$, $CH_4 + 6O_2$, and $C_2H_2 + O_2$ as initiators. The velocity in any given mixture was found to be independent of the particular initiator used.

The apparatus was as follows: A steel firing piece at the closed end of the tube system was attached by a screw-thread to a 3-m. length of Cu tube; then followed 225 cm. of glass tubing, in the final 150 cm. of which the velocity measurements were made. This was followed by a

FIG. 1.



length of tubing (in some expts. of Pb 5 m. long, and in others of glass 2·4 m. long) bent round and terminating in a second 150-cm. length of glass tubing, placed immediately below the previous one. This second glass tube enabled a further velocity measurement to be made. The tubes were all 1·5 ± 0·05 cm. in bore and special care was taken to make the joints between the various sections of the gallery smooth and rigid.

The flames were photographed on a drum camera accurately alined with the tubes and rotated at a known peripheral speed of about 80 m./sec. If the photographic trace due to the flame front was perfectly straight, it was assumed that detonation had been fully established in the mixture.

All the mixtures used, except $C_2H_2 + O_2$, were stored over H_2O at *ca.* 15° and, after standing several hours, were, in general, led straight to the explosion gallery. They contained not more than 1% of N. In a few cases the mixtures from the gas-holders were passed through several $CaCl_2$ drying tubes. No difference in velocity was obtained between the " dry " and the moist mixtures, although similar variation in moisture content is known to have a marked effect on the initial speed of inflammation (Payman and Wheeler, J., 1932, 1835).

The results are in Table I, and in most cases velocities are given for the two glass tubes. In those cases where no velocity is recorded for the first glass tube, detonation had not been fully established when the flame entered the tube; the flame either traversed the tube as a " slow flame " or gave place to detonation at some point along its length. The second glass tube was not used in all the expts.

The mean velocities for the different mixtures are plotted against their compositions in Fig. 1. The curve indicates that there is an almost linear increase in velocity from 1710 m./sec. for the mixture containing 50% to 1770 m./sec. for that containing 80% CO. The increase is small—only 60 m./sec.—and there is no evidence from the curve, or from individual results, that there is a sudden increase in velocity with any given mixture. A similar smooth curve, showing

an approx. linear relationship between velocity and compn. over the main portion of the range of detonation, has been found for mixtures of CH_4, C_2H_4, C_2H_2, C_5H_{12}, C_6H_6, $(CN)_2$, or H with O (Dixon, *loc. cit.*).

TABLE I.

Rates of detonation in carbon monoxide–oxygen mixtures with initiation by "electrolytic firing."

CO, %.	Initiating mixture.	Velocity (m./sec.). 1st Glass tube.	2nd Glass tube.	Mean.
50·0	$2H_2 + O_2$	1710		1710
55·1	$2H_2 + O_2$	1708	1723	1716
60·2	$2H_2 + O_2$	1765	1735	
	,,	1730	1735	1736
	,,	1722	1730	
63·7	$C_2H_2 + O_2$	1737	—	
	,,	1737	1737	1746
	,,	1780	1740	
66·2	$CH_4 + 6O_2$	1740	—	
	,,	1758	1758	1752
67·6	$C_2H_2 + O_2$	1750	1750	
	,,	—	1755	
	$2H_2 + O_2$	1757	1770	1757
	,,	1757	—	
74·4	$2H_2 + O_2$	—	1770	1770
75·7	$C_2H_2 + O_2$	1770	1770	
	,,	—	1755	1761
	,,	—	1750	
77·6	$C_2H_2 + O_2$	—	1790	
	$2H_2 + O_2$	1770	1770	1768
	,,	—	1763	
	,,	—	1750	
79·7	$C_2H_2 + O_2$	1755		
	,,	1770		
	,,	1775		
	,,	1762		1768
	,,	—	1760	
	,,	—	1765	
	$2H_2 + O_2$	1770	1790	
83·0	$C_2H_2 + O_2$	1715		1714
	,,	1712		

In all cases the curves show a max. for one particular mixture; further addition of combustible gas results in diminished velocity. With H and CO mixtures the max. is very ill-defined and this, in the case of H, is known to be in accord with calculations. Below are given the velocities in H–O mixtures calculated by Jouguet's method (*J. Math.*, 1905 and 1906), and these are compared with the velocities observed by Dixon (*loc. cit.*) in Pb tubes of 9 mm. and 13 mm. bore. In view of the recent results of Bone and Fraser (*loc. cit.*), velocities in a 15-mm. tube may all be slightly higher.

Explosion-wave velocities in hydrogen–oxygen mixtures (m./sec.).

H_2, %	80·0	85·7	88·9	90·0	90·9	91·7	92·3	93·3
Obs. (Tube bore 9 mm.) ...	3268	3527						
,, ,, ,, 13 ,, ...			3532					
Calc.	3300	3530	3550	3590	3620	3610	3600	3590

The calc. agree well with the obs. values where comparison is possible and show that with H there may be an ill-defined max. Since these calculations are based solely on the assumption that the reaction occurring is $2H_2 + O_2 = 2H_2O$, it follows that the max. is merely due to the fact that at some point the increase in velocity due to the addition of the lighter gas, H, is more than counterbalanced by the diminution in velocity due to the reduction in the heat available.

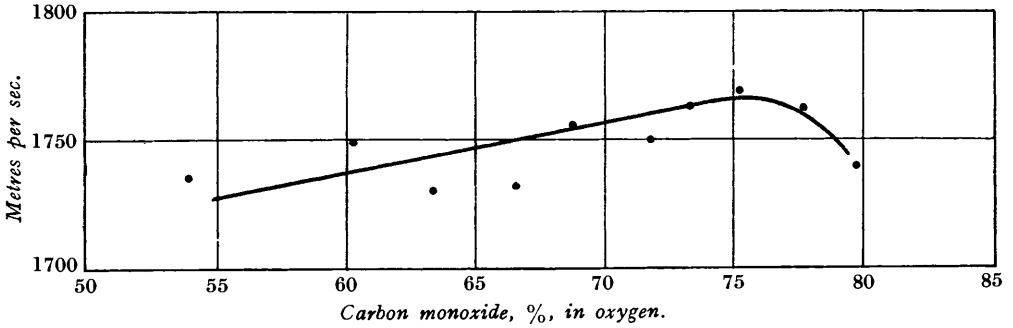
There seems no reason to think that a similar explanation cannot also account for the observed velocities in CO–O mixtures. Moreover, since the density of CO is only slightly less than that of O, any max. might be still more ill-defined than in the case of H. Beyond the max., the limit of detonation is almost reached, which probably explains the rapid fall in velocity shown by the values in Table I. There is some divergence between the velocity observed in the mixture $2CO + O_2$ and that calculated by Jouguet's method, which, as we have shown recently (*Proc. Roy. Soc.*, **1932**, **137**, *A*, 380), may be due to uncertainties in the sp. heats and in the validity of the gas laws at the temp. of the reaction. In $2CO + O_2$ the calc. velocity is 1660 m./sec., or 90 m./sec. below the obs. velocity, 1750 m./sec. But throughout the detonating range there is a close similarity in the differences between the calc. and the obs. velocities; *e.g.*, in $3CO + O_2$ the calc. and obs. velocities are 1710 and 1770 m./sec., respectively.

Whilst this explanation seems quite adequate to explain our results, an alternative point of view has recently been put forward by Bone and Fraser (*Proc. Roy. Soc.*, **1931**, **130**, *A*, 542). They suggest that "in the case of moist carbonic oxide–oxygen mixtures the point of maximum flame speed is principally determined, not by the density of the medium, nor by the flame temperature, nor yet by the suppression of CO_2-dissociation nor the like, but rather by the

CO concentration itself. And such a conclusion points to the combustion of moist carbonic oxide being conditioned by a prior excitation of its molecules, which are then, but not otherwise, rendered combustible." This conclusion was supported by their exptl. results, which show a marked maximum speed with about 75% CO, the speed–composition curve exhibiting a sharp peak at that percentage. A few relatively high values also appear in our results, but since it has not been possible to reduce the exptl. error below 1%, we believe that no conclusions should be drawn from these individual results and that the smooth curve drawn through the mean velocities for each different mixture is a more correct representation of the facts. No sharp peak is disclosed by this curve at 75% CO and since the only important difference in exptl. method was the mode of initiation of detonation, it appeared desirable to extend our experiments by using a detonating box and 12·5-mm. tube similar to those used by Bone and Fraser.

The arrangement of the explosion tube was as follows: A short ebonite tube containing a spark gap was attached to one end of the rectangular detonating box, which was constructed of a series of flat brass plates. To the other end of the box was screwed a steel tube, 12·5 mm. in internal diameter and 3·2 m. long, to which was jointed the glass tube, 1 m. long, in which the flame was photographed. The action of the detonating box appears to be the provision of a series of shock waves, set up after the initial inflammation of the gas, which give rise to rapid successive accelerations of the flame, thereby leading very quickly to the establishment of detonation. The results of the determinations using this method of initiation are given in Table II. The mean values, which are plotted in Fig. 2, are more variable than those in Fig. 1. However,

FIG. 2.



the agreement with our earlier values is satisfactory, although the short downward bend of the curve after the max. velocity begins at a slightly lower percentage of CO. There is no pronounced peak at the 75% CO mixture.

TABLE II.

Rates of detonation in carbon monoxide–oxygen mixtures with initiation by "detonating-box."

CO, %.	Velocity (m./sec.).	Mean.	CO, %.	Velocity (m./sec.).	Mean.	CO, %.	Velocity (m./sec.).	Mean.
54·0	1735	1735	68·8	1767		75·2	1764	
60·3	1749	1749		1745	1756		1786	1769
63·4	1730	1730		1755			1772	
66·6	1731	1736	71·8	1750	1750		1756	
	1740		73·3	1763	1763	77·7	1766	1762
							1758	
						79·7	1740	1740

SUMMARY.

The rates of detonation of various mixtures of carbon monoxide and oxygen have been determined. As for many other detonating gas mixtures, the speed–composition curve shows an almost linear increase of speed with increase in percentage of combustible gas over most of the detonating range; and, as with hydrogen–oxygen mixtures, the speed appears to be determined mainly by the calorific value and density of the mixture.

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