Chemical Reaction in a Shock Wave. I. The Ignition Delay of a Hydrogen-Oxygen Mixture in a Shock Tube

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Many studies have been published about the reaction of hydrogen-oxygen mixtures.[1-4] In order to clarify the mechanism of this reaction, measurements of the induction period, during which the extent of reaction cannot be detected by the measuring instrument, are very useful.[*,5] Measurements of this induction period at low temperatures and low pressures have been already published[5] and those at high temperatures and low pressures have been conducted by Schott and Kinsey[3] and by Strehlow.[4]

In order to ignite the combustible mixture, there are various methods, such as ignition by electric spark,[6,7] by compression waves,[8] and by hot surfaces and by hot wires.[9] However, the shock-tube technique is most useful for the measurement of the induction period or ignition delay, because the shock wave heats the mixture to a desired temperature almost instantaneously and homogeneously.

In the present experiment, the author tried to measure the induction period of a hydrogen-oxygen mixture in a shock tube at a moderate temperature and a rather high pressure ($825 \leq T_r \leq 1360°K$, $670 \leq P_r \leq 2670$ mmHg and $7.6 \times 10^{-4} \leq [O_2] \leq 3.0 \times 10^{-3}$ mol./l.) ; he tried also to examine the mechanisms proposed by other authors, whose measurements have been conducted under different conditions.

Experimental

The shock tube,[10] made from mild steel, has a square cross section with an inside lateral of 5 cm. and is divided into two sections, the reservoir chamber, A, 60 cm. in length and the test chamber, C, 180 cm. in length. Chambers A and C are separated by several sheets of cellophane film which can be punctured by the needle, N.

(a) (b)

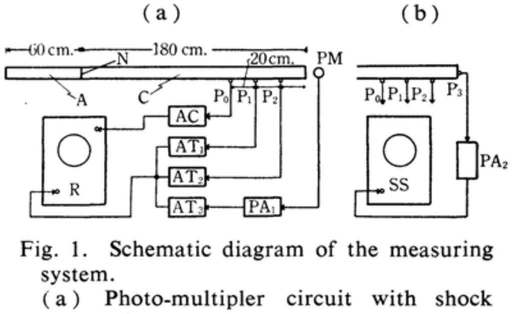


Fig. 1. Schematic diagram of the measuring system.
(a) Photo-multipler circuit with shock tube
(b) Piezo-gauge circuit, otherwise similer to (a)

1) M. Steinberg and W. E. Kaskan, "5th Symposium on Combustion," Baltimore, The Williams and Wilkins Co., (1955), p. 664.

* For example, Schott et al.[3] defined this period as the time during which the OH concentration reaches the threshold of detectability.

2) J. A. Fay and E. Lekawa, *J. Appl. Phys.*, **27**, 261 (1956).

3) G. L. Schott and J. L. Kinsey, *J. Chem. Phys.*, **29**, 1177 (1958).

4) R. A. Strehlow, presented before the Division of Fuel Chemistry, American Chemical Society, St. Louis, Missouri, March, 1961.

5) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. II., Princeton Univ. Press, Princeton, New Jersey (1959), p. 163.

6) M. V. Blane, P. G. Guest, G. von Elbe and B. Lewis, *J. Chem. Phys.*, **15**, 798 (1947).

7) W. Roth, P. G. Guest, G. von Elbe and B. Lewis, ibid., **19**, 1530 (1951).

8) B. P. Mullins, "Spontaneous Ignition of Liquid Fuels," Butterworths, London (1955), p. 13.

9) W. Jost, "Explosions und Verbrenunggsvorgänge in Gasen," Springer, Berlin (1939). p. 36.

10) M. Suzuki, H. Miyama and S. Fujimoto, This Bulletin, **31**, 819 (1958).

A brief scheme of the measuring system is shown in Fig. 1. As the shock wave passes down the tube, a signal on the piezo gauge, P_0, is thereby actuated; this signal is amplified through the amplifier circuit (AC) and triggers a raster-oscilloscope, Type SS 5101, made by the Iwasaki Communication Apparatus Co., which can respond to a time up to 1 μsec. The subsequent piezo gauges, P_1 and P_2, are actuated by the downward travelling shock wave, and the signals are fed through amplifier thyratron circuits (AT_1) and (AT_2), again on the raster-oscilloscope, thus providing a measurement of the incident shock speed. The measurement of the ignition was made in two ways. One method depends upon a raster-oscilloscope pattern actuated by a photo-multiplier (Fig. 1-(a)). A light signal initiated by the light emission of the gas mixture passes through a transparent plastic window, hits a photo-multiplier tube, and, appears in the sweep on the raster-oscilloscope, thus making possible an estimation of the exact time of ignition. A sample raster-oscilloscope pattern is shown in Fig. 2.

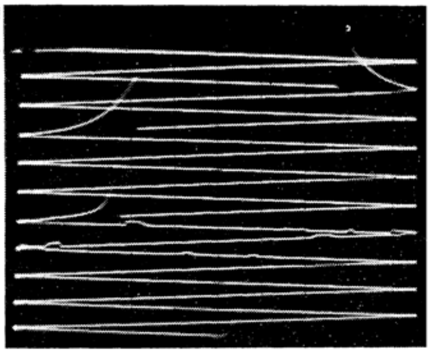
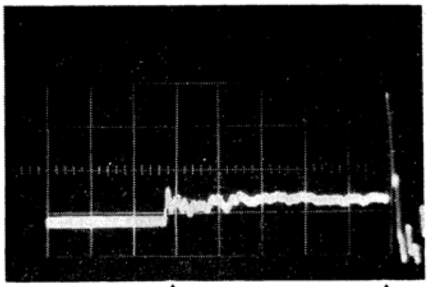


Fig. 2. Raster-oscilloscope diagram (an example).
N_2; 80%Ar+20%($2H_2+O_2$)
ω=740 m./sec., τ=298 μsec.
The 1st and 2nd signals are those from velocity gauges and 3rd signal is from photomultiplier gauge.

In the second method, measurements are carried out by using a piezo-gauge placed at the bottom of the shock tube. A pressure disturbance, accompanied by gas detonation, through a preamplification circuit (PA_2) (Fig. 1-(b)), gives a relevant pressure pattern on a synchroscope (Type 5302 of the Iwasaki Communication Apparatus Co.); this enables one to determine the exact time of the ignition. A sample pattern is given in Fig. 3. Both methods were applied for each run of measurements; the results obtained from the two ways were satisfactorily concordant. Piezogauges have been used by several investigators in shock studies.[11,12] A gauge of this type, made in this laboratory, has proven eminently successful as a detector of weak shock waves.

11) W. W. Willmarth, *Rev. Sci. Inst.*, **29**, 218 (1958).
12) B. Greene and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **72**, 1080 (1950).



↑ Reflected shock wave ↑ Start of ignition

Fig. 3. Synchroscope pattern of a signal from the piezogauge on the bottom of the shock tube.
N_2; 70%Ar+30% ($2H_2+O_2$)
ω=733 m./sec., τ=530 μsec.

As a driver gas in the reservoir, A, nitrogen was used. In the test chamber, C, $0.067H_2+0.033O_2+0.900Ar$, $0.133H_2+0.067O_2+0.800Ar$ and $0.2H_2+0.1O_2+0.7Ar$ were used. In the present report, only ignitions caused by reflected shock waves will be described.

Results and Discussion

From Fig. 2, where a sample of a raster-oscilloscope diagram is shown, the incident shock velocity, ω, and ignition delay, τ, at various shock conditions can be obtained; they are tabulated in Tables I and II. For the evaluation of the τ values, it is assumed that the ignition occurs at the wall of the end plate of the shock tube; a Schlieren picture taken by Strehlow[4] seems to justify this assumption. Applying the usual process

TABLE I. VALUES OF ω, τ, T_r, P_r, and O_2 FOR 70%Ar+30%($2H_2+O_2$) PHOTO-MULTIPLIER METHOD

P_1 mmHg	ω m./sec.	τ μsec.	T_r °K	P_r mmHg	O_2 mol./l. $\times 10^3$
100	666	2227	825	1208	2.348
50	683	2019	870	673	1.241
50	692	1525	891	702	1.264
50	703	1302	909	734	1.295
50	707	1059	918	750	1.310
50	719	1014	945	789	1.340
50	736	888	987	847	1.376
50	764	543	1053	955	1.455
50	797	177	1131	1074	1.525
50	830	156	1215	1223	1.616
50	840	130	1242	1266	1.635
50	844	143	1254	1286	1.647
50	851	115	1269	1317	1.665
50	862	109	1308	1373	1.685
50	870	117	1323	1408	1.708
50	885	84	1362	1478	1.740

TABLE II. VALUES OF ω, τ, T_r, P_r AND O_2 FOR $70\%Ar+30\%(2H_2+O_2)$ PIEZOGAUGE METHOD

P_1 mmHg	ω m./sec.	τ μsec.	T_r °K	P_r mmHg	O_2 mol./l. $\times 10^3$
100	694	1220	894	1416	2.540
100	709	1142	924	1511	2.622
100	717	1164	942	1565	2.655
100	722	1120	948	1577	2.670
100	725	1020	960	1618	2.701
100	733	958	978	1672	2.741
100	735	630	984	1686	2.749
100	740	624	996	1730	2.785
100	744	160	1008	1765	2.810
100	746	158	1010	1775	2.814
100	749	190	1017	1800	2.840
100	752	179	1026	1818	2.841
100	754	160	1029	1835	2.860
100	763	120	1050	1905	2.910
100	769	154	1065	1949	2.935
100	772	126	1071	1975	2.960
100	773	120	1074	1982	2.962
100	778	138	1086	2020	2.988

of calculation,[13] the temperature, T_r, and the pressure, P_r, of the reflected shock wave and the concentration of oxygen behind the reflected shock wave are also tabulated in Tables I and II. In this procedure, a constant value of γ is assumed.*1

Steinberg and Kaskan[1] found a linear relationship between $\log_{10}\tau$ and $1/T_r$ for a $2H_2+O_2$ mixture without dilution. Schott and Kinsey[3] measured the formation of OH in the shock wave-induced combustion of H_2 and O_2 by using the ultraviolet absorption of OH and found a linear relationship between $\log_{10}\tau[O_2]$ and $1/T$ as follows:

$$\log_{10}\tau[O_2] \text{ (mol. l}^{-1}\text{ sec.)} = -10.647+(3966\pm625)/T \quad (1)$$

Strehlow[4] obtained a similar result by using a conventional shock tube and the Schlieren system. In comparison with their results, our results are shown in Fig. 4. Although the position of our least square line is different from that of the other authors, the slope of the line is about the same. The least square line is expressed as follows;

$$\log_{10}\tau[O_2] \text{ (mol. l}^{-1}\text{ sec.)} = -9.581+3559/T_r \quad (2)$$

The difference in the position of lines can not be explained as arising from experimental error, because the uncertainty of the τ value is less than 1 μsec. and that of T_r, less than 1%.*2

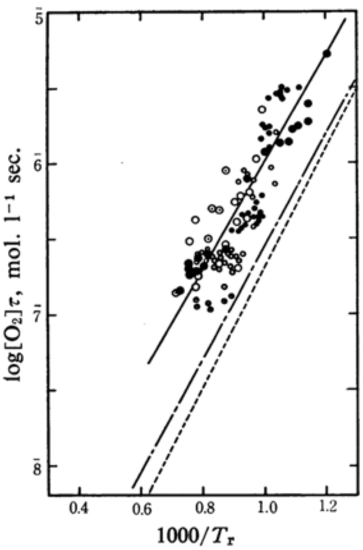


Fig. 4. Relation between $\log_{10}[O_2]\tau$ and $1/T_r$ for $2H_2+O_2$ with argon.

	Photo-multiplier method	Piezo gauge method
$70\%Ar+30\%(2H_2+O_2)$	●	●
$80\%Ar+20\%(2H_2+O_2)$	○	○
$90\%Ar+10\%(2H_2+O_2)$	⊙	⊙
Strehlow's line	——·——·——	
Schott's line	-------------	

In order to explain the induction time, τ, Semenov assumed the following reactions:

$$OH + H_2 \rightarrow H_2O + H \quad (I)$$

$$O_2 + H \rightarrow OH + O \quad (II)$$

$$O + H_2 \rightarrow OH + H \quad (III)$$

Schott and Kinsey[3] also adopted Semenov's mechanism and derived the similar equation:

$$\tau[O_2] \propto \frac{1}{k_2} = \exp(E_2/RT)$$

In the derivations described above, Reaction IV is disregarded because of its low reactoin velocity compared with that of reaction II.

$$H + O_2 + M \rightarrow HO_2 + M \quad (IV)$$

If reaction IV is taken into account, the following relation is derived:

$$\tau[O_2] \propto \frac{1}{k_2\{1-k_4[M]/2k_2\}}$$

13) I. I. Glass, W. Martin and G. N. Patterson, "A Theoretical and Experimental Study of the Shock Tube," UTIA Report No. 2, November, 1953.

*1 In the present experiment, the hydrogen-oxygen mixture is diluted with argon and the temperature is not very high. Therefore, the variation of γ with the temperature is not so large as to decrease the value of T_r beyond the range of experimental error.

*2 This uncertainty is guessed from the accuracy of the measuring instrument. However, according to the experimental results, the fluctuation of τ at a definite temperature is $\pm 8\%$ and the fluctuation of T_r at a definite τ value is $\pm 5\%$.

Under the experimental conditions of Schott and Kinsey[3] $k_4[M]/2k_2$ is far less than 1 and the $\tau[O_2]\propto(1/k_2)$ relation may be applied. However, under the present experimental conditions, where pressure is comparatively high and temperature is low, $k_4[M]/2k_2$ can not be ignored in comparison with 1. According to Lewis and von Elbe,[14] $2k_2/k_4[M]$ is expressed as follows;

$$2k_2/k_4[M]=\frac{0.0556}{f_{H_2}+0.35f_{O_2}+0.20f_{Ar}}\times\frac{T}{P}\times\exp-\left[\frac{17000}{803R}\left(\frac{803}{T}-1\right)\right]$$

where is the mole fraction of the components of the mixture, P is the pressure in mmHg, and T is the absolute temperature. By using this equation, $k_4[M]/2k_2$ under the present experimental conditions can be calculated as follows.

T, °K	$k_4[M]/2k_2$
900	1.64
1000	0.69
1100	0.35
1200	0.20
1300	0.14

Obviously, $k_4[M]/2k_2$ is not ignored, and, therefore, reaction IV must be taken into consideration. However no quantitatively satisfactory explanation for the difference between our data and that of the others shown in Fig. 4 has yet been obtained. Also, it is difficult to explain why the value, 16.3 kcal., of the activation energy obtained by using the slope of the line in Fig. 4 is very close to those of Schott (18.1 kcal.) and Strehlow (16.5 kcal.). It is supposed that the simple scheme described above does not express the situation correctly.*3 In order to obtain a fully satisfactory explanation, it is necessary to conduct a more detailed study.

Summary

The values of the ignition delay of a hydrogen-oxygen mixture with a diluent in the reflected shock waves were measured by using a shock tube equipped with a piezo gauge for shock velocity measurements and a photomultiplier or another piezo gauge for the measurement of the time of ignition.

There was the following relationship between the ignition delay, τ, and the temperature, T_r, behind the reflected shock wave:

$$\log_{10}\tau[O_2]\ (\text{mol. l}^{-1}\ \text{sec.})=-9.581+3559/T_r$$

where $825\leq T_r\leq 1360$°K and $7.6\times10^{-4}\leq[O_2]\leq 3.0\times10^{-3}$ mol./l. The difference between this relationship and that set forth by other authors has been discussed.

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14) B. Lewis and G. von Elbe, "Combustion Flams and Explosions of Gasee," Academic Press Inc., New York (1961), p. 45.

*3 According to Dr. W. C. Gardiner's private communication to Dr. H. Miyama, it appears that there are three reactions in the induction time that have almost the same rate constants.