A Shock-Tube Study of the Acetylene-Oxygen Reaction

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(Received October 2, 1964)

Kistiakowsky and his collaborators have extensively investigated the acetylene-oxygen reaction in shock waves, using a wide variety of techniques to follow reaction processes, i. e., mass spectrometry,[1] X-ray densitometry,[2] vacuum ultraviolet emission spectroscopy,[3] and Langmuir probe technique.[4] They proposed that the rate of the main process operating in the induction period is determined by the reaction, $H+O_2 \rightarrow OH+O$, as in the hydrogen-oxygen reaction.

Observing visible or ultraviolet emission and OH absorption simultaneously, Stubbeman and Gardiner[5] have recently found that OH appears much later than the emission pulse and have explained that the high reactivity of OH is responsible for its delayed appearance. Since both Kistiakowsky's group and Stubbeman and Gardiner studied the reaction at higher temperatures and lower pressures, it now seems worth while to study the reaction under conditions similar to those chosen by us for the hydrogen-oxygen reaction,[6] i. e., at lower temperatures and higher pressures.

In this paper we will report the results obtained from simultaneous measurements of OH absorption, visible emission and pressure over the temperature range 820−1630°K and the pressure range 1.8−5.6 atm.

Experimental

Shock Tube and Instrumentation. — The shock tube used was the same one as that described previously[7] except for a minor change in the observation system : an auxiliary observation station for emission measurement was installed in the lower part of the tube 5.5 mm. from the end plate, the same position as that for OH absorption and pressure measurement. For experiments in incident stock waves, a 1.2 m. tube of the same diameter was connected to the downstream end. A Shimadzu QR-50 monochromator with an R 106 photomultiplier (Hamamatsu TV Company) was used to isolate spectral regions of light transmitted through or emitted from the shock-heated gas at the principal observation station. The width of the exit slit of the monochromator was set at 0.15 mm. for the OH absorption measurement and at 0.50 mm. for the visible emission, the band widths being 7 and 65 Å respectively. The induction period for the onset of visible emission was measured by an 1P28 photomultiplier placed 30 cm. under the tube ; the optical system consisted of a quartz window, a 1 mm. wide slit, an interference filter (Vacuum Optics Corporation of Japan) (peak 4305 Å ; half-band width of 65 Å ; peak transmission 52%), a 1 mm. wide slit, and an 1P28 photomultiplier. A quartz-pressure transducer (Kistler model 603) was used for the pressure measurement 5.5 mm. from the end plate. Two platinum-film resistance thermometers and an electronic counter (Takeda Riken 4247) were used to measure the shock velocities.

The Calculation of Shock Parameters.—Temperatures, pressures and other parameters of the gas behind the incident and reflected shock waves were calculated by means of the one-dimensional theory described in a previous paper.[7]

Materials.—Matheson acetylene (99.66% min.) was used after being passed through two dry ice traps and having been determined to be free from acetone by a mass spectrometer. Nippon Sanso oxygen (99.5% min.) and argon (99.999% min.) were used without further purification.

Results

The Measurement of the Induction Period.— By using reflected or incident shock waves, the induction periods for the OH appearance, the onset of visible emission and the pressure increase were measured simultaneously at the same location in the tube. The experimental conditions are summarized in Table I.

TABLE I. SUMMARY OF EXPERIMENTAL CONDITIONS

Mixture	% Ar	$[C_2H_2]/[O_2]$	Temp. range °K	$[O_2]$ range 10^{-3} mol./l.
I	90	0.67	820—1300	1.63—4.08
II	93	0.40	970—1630	1.13—1.86
III	95	1.5	1110—1480	0.842—1.21
IV	94	1.0	1130—1520	1.16—1.76

A sample of the oscillograms obtained is shown in Fig. 1. The OH appearance, the onset of visible emission and the increase in

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[1] J. N. Bradley and G. B. Kistiakowsky, *J. Chem. Phys.*, **35**, 264 (1961).
[2] W. C. Gardiner, Jr., ibid., **35**, 2252 (1961).
[3] G. B. Kistiakowsky and L. W. Richards, ibid., **36**, 1707 (1962).
[4] C. W. Hand and G. B. Kistiakowsky, ibid., **37**, 1239 (1962).
[5] R. F. Stubbeman and W. C. Gardiner, Jr., ibid., **40**, 1771 (1964).
[6] H. Miyama and T. Takeyama, ibid., **41**, 2287 (1964).
[7] H. Miyama and T. Takeyama, This Bulletin, **38**, 37 (1965).

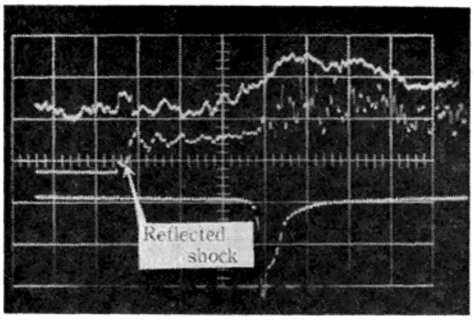

Fig. 1. Sample oscillogram. Mixture I, initial pressure 109.8 mmHg, shock temperature 1060°K, sweep rate 100 μsec./division. Top trace represents OH absorption, middle trace pressure change and bottom trace emission at 4320 Å.

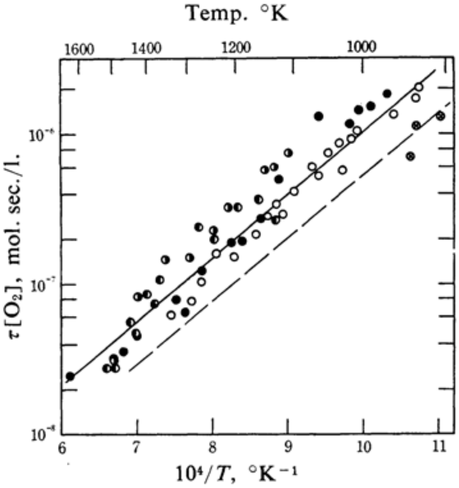

Fig. 2. Induction periods for appearance of OH absorption. Solid line is the least-squares line through the points and dashed line is the one obtained in the hydrogen-oxygen reaction.[6] The points are identified as follows:

Symbol	Mixture	Type of shock
○	I	reflected
⊗	I	incident
●	II	reflected
◑	III	reflected
◐	IV	reflected

pressure occurred almost concurrently after an induction period, τ, over the whole temperature range studied. In Fig. 2, the results for τ measured by OH absorption spectroscopy are shown as a plot of $\log(\tau[O_2])$ vs. $1/T$. The induction periods measured in incident shock experiments were multiplied by the density ratio in order to convert the laboratory time into particle time. Although there are few data from incident shock experiments because of the experimental difficulties encountered, the data we do have fall close to those obtained from reflected shock experiments. It should also be noted that, over the 0.4—1.5 range of acetylene to oxygen ratio there exists a linear relationship between $\log(\tau[O_2])$ and $1/T$; hence, the induction periods are dependent upon the oxygen concentration, as has been reported in the literature.[3,4] The equation of the least-squares line through these points is:

$$\log(\tau[O_2])\ (\text{mol. sec./l.}) = -10.16\pm0.15+(4160\pm140)/T \tag{1}$$

The dashed line in Fig. 2 is the least-squares line obtained by us in the hydrogen-oxygen reaction.[6]

The Intensity Distribution of Visible Emission.—In order to identify the visible emitter, the intensities of emission were measured with the monochromator which had been used for OH absorption spectroscopy; 80 mmHg of gas mixture I (see Table I) was heated by reflected shock waves to 1210±30°K, and the wavelength setting of the monochromator was varied from run to run through the region 4100—4500 Å. The intensities measured were corrected with the spectral response of the R106 photomultiplier; they are shown in Fig. 3. There exists a sharp peak at about 4320 Å.

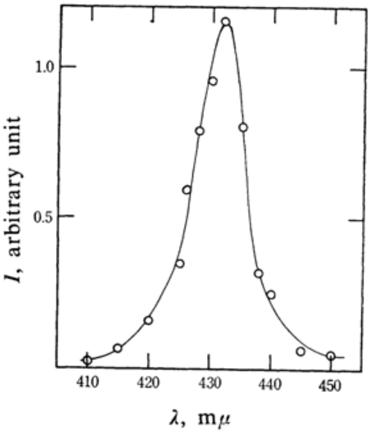

Fig. 3. Emission intensity vs. wavelength.

The Temperature Dependence of the Intensity of Visible Emission.—The intensities of visible emission were measured at 4200, 4320 and 4450 Å over the temperature range 900—1270°K by using 80 mmHg of gas mixture I (see Table I) as the driven gas and 2.8—3.2 atm. of helium as the driver gas. The results are shown in Fig. 4. Although the intensities observed at 4200 and 4450 Å are almost independent of the temperature those at 4320 Å show a slight dependence, one which corresponds to an activation energy of about

6 kcal./mol. In these experiments, the concentrations of oxygen were kept nearly constant, ranging from 1.19×10^{-3} to 1.58×10^{-3} mol./l.; hence, it can be considered that no factors other than the temperature are involved in the results shown in Fig. 4.

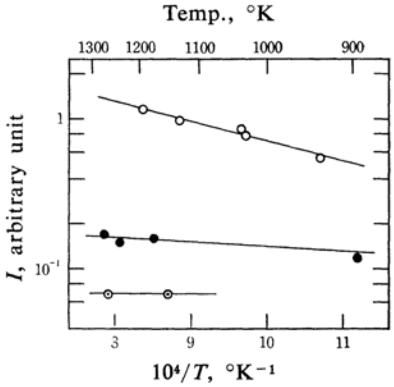

Fig. 4. Emission intensity vs. reciprocal temperature. Intensities measured at 432, 420 and 445 mμ are represented by ○, ●, and ⊙, respectively.

Ionization.—In the course of incident shock experiments, the output signals from the thin-film thermometers were found to be unreasonably delayed when the shock Mach number was increased. The oscillogram of these outputs revealed, as Fig. 5 shows, that negative signals occur when the shock front passes the thermometers and that the increase in the resistances of the thermometers due to temperature rise are delayed a few hundred micro seconds. This anomaly is attributable to the ionization of gases surrounding the thermometers ; it was therefore considered necessary to examine the details of ionization.

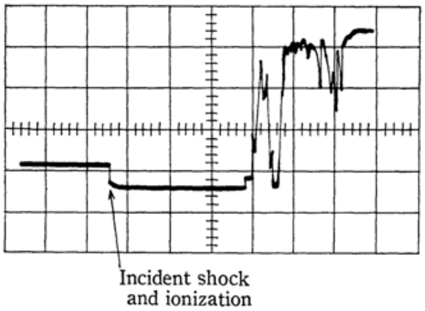

Fig. 5.—Oscillogram of thin-film thermometer showing ionization on arrival of shock. Mixture I, initial pressure 70.7 mmHg, shock temperature 1210°K, sweep rate 200 μsec./division.

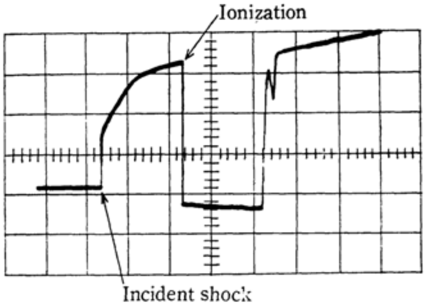

Fig. 6. Oscillogram of thin-film thermometer showing induction period for ionization. Mixture I, initial pressure 87.6 mmHg, shock temperature 920°K, sweep rate 200 μsec./division.

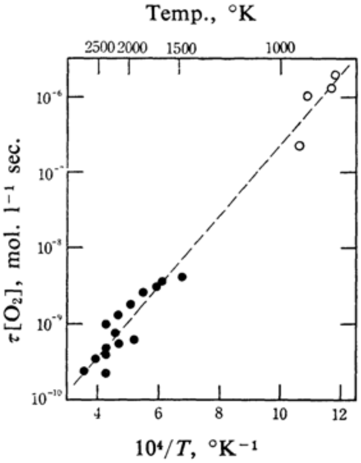

Fig. 7. Induction periods for ionization. Open circles are obtained in the present study with thin-film thermometer and solid circles by Hand and Kistiakowsky with Langmuir probe.

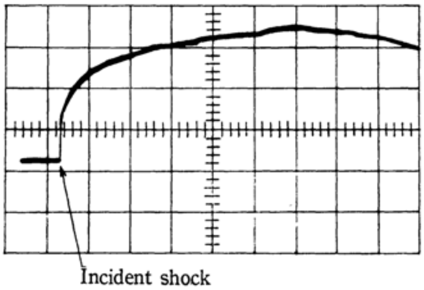

Fig. 8. Oscillogram of thin-film thermometer showing no ionization. Argon, initial pressure 20.0 mmHg, shock temperature 2030°K, sweep rate 100 μsec./division.

A series of experiments was conducted using 100—40 mmHg of mixture I (see Table I) as the driven gas and 5 atm. of helium as the driver. The temperature range thus covered was 850—1200°K. According to the oscillograms obtained at temperatures higher than 1030°K, i. e., $P_1\leq83$ mmHg, the ionization begins as soon as the shock front has arrived.

However, below this temperature the ionization occurs after an induction period, as Fig. 6 shows. This induction period is of the same order of magnitude as that measured by the pressure transducer at the same time, and it becomes longer as the temperature is lowered. In Fig. 7, the present results are compared with those of Hand and Kistiakowsky (cf. Fig. 4 of their paper[4]). The present data fall just on the line which is an extrapolation of theirs. For purposes of comparison, a strong shock was generated in 20 mmHg of argon or air. No ionization was found in these cases, as is shown in Fig. 8, although the temperatures were much higher than those for the cases where ionization was found in an acetylene-oxygen mixture.

Discussion

Kistiakowsky and his collaborators[1,3] proposed the following scheme as operating during the induction period of acetylene-oxygen reaction in shock waves:

$$H+O_2 \rightarrow OH+O \qquad \Delta H=17\ \text{kcal./mol.} \qquad \text{(I)}$$

$$O+C_2H_2 \rightarrow C_2H+OH \qquad \Delta H\leqq 20\ \text{kcal./mol.} \qquad \text{(II)}$$

$$OH+C_2H_2 \rightarrow C_2H+H_2O \qquad \Delta H\leqq 1\ \text{kcal./mol.} \qquad \text{(III)}$$

$$C_2H+C_2H_2 \rightarrow C_4H_2+H \qquad \Delta H=-23\ \text{kcal./mol.} \qquad \text{(IV)}$$

Reaction I was considered to be rate-controlling, since the induction period behaves very similarly to that in the hydrogen-oxygen reaction.[8]

The present results shown in Fig. 2 do indicate that, in the range of conditions $820^\circ \leqq T \leqq 1630^\circ$K, $1.8 \leqq P \leqq 5.6$ atm., $8.4\times10^{-4} \leqq [O_2] \leqq 4.1\times10^{-3}$ mol./l., and $0.4 \leqq [C_2H_2]/[O_2] \leqq 1.5$, the induction period depends upon the oxygen concentration and that the activation energy derived from Eq. 1 is 19.0 ± 0.6 kcal./mol. Furthermore, the present data fall close to those obtained by us for a hydrogen-oxygen reaction.[6] Thus, reaction I is also rate-determining under the conditions of the present study.

In the hydrogen-oxygen reaction,[6] it was found that the induction period for an abrupt increase in pressure is much longer than that for OH absorption at temperatures below about 1100°K, and that it depends on the hydrogen rather than on the oxygen concentration. These findings were attributed to the participation of HO_2 radicals in the reaction processes at lower temperatures. However, the present study of the acetylene-oxygen reaction revealed no such effects. It is probably due to exothermic side reaction,[9] which prevent the accumulation of HO_2 radicals.

Although Stubbeman and Gardiner[5] found that the OH appearance is much later than the emission and ascribed it to the high reactivity of OH radicals, the present study has shown that OH absorption, visible emission and pressure increase occurred simultaneously over the whole temperature range studied. Since OH absorption increases much less rapidly than visible emission, as Fig. 1 shows, the induction period for the appearance of OH absorption is much more dependent upon such experimental conditions as the pressure, temperature, and the detectability of the measuring system. Therefore, we would explain the discrepancy between the present results and those of Stubbeman and Gardiner on the grounds of difference in facilities for detecting OH radicals.

Glass[10] has inferred from experiments with several interference filters that there should be a peak at about 4300 Å, and he has suggested that the principal emitter of visible radiation must be the CH radical instead of the reaction $CO+O \rightarrow CO_2+h\nu$ proposed by Stubbeman and Gardiner.[5] The present results obtained with a monochromator give strong evidence, as Fig. 3 shows, that there is a sharp peak at about 4320 Å. Accordingly, the visible emission observable in the acetylene-oxygen reaction in shock waves can be assigned to the $^2\Delta\rightarrow{}^2\pi$ transition of CH, as is the case with hydrocarbon-oxygen flames.[11] The probable reactions which cause chemiluminescence are considered to be:

$$C_2H+O_2 \rightarrow CO_2+CH^* \qquad \text{(V)}$$

or:

$$C_2H+O \rightarrow CO+CH^* \qquad \text{(VI)}$$

However, it is impossible to decide on the basis of the present results which of these is predominant.

The temperature dependence of the maximum intensity in Fig. 4 corresponds to 6 kcal.; it is much smaller than the energy required for placing the CH radical in the $^2\Delta$ state (66.6 kcal.). Therefore, as has been suggested for vacuum ultraviolet emission and ionization,[4] a high collisional yield must be assumed in order to explain the strong visible emission.

The ionization encountered in the course of

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

9) W. C. Gardiner, thesis, Harvard University, 1960.

10) G. P. Glass, private communication.

11) A. G. Gaydon, "The Spectroscopy of Flames," Chapman & Hall, London (1957), pp. 113—135, 234—245.

incident shock experiments is apparently chemical in origin, since it was observed only in the case of the acetylene-oxygen mixture and since, moreover, the induction period for ionization was of the same order of magnitude as that for the pressure increase. As is shown in Fig. 7, this chemi-ionization should be essentially the same as that observed by Hand and Kistiakowsky[4] with a Langmuir probe, and the reaction

$$CH^* + O \rightarrow CHO^+ + e^-$$

should be responsible. Thus, it is prospective to use a thin-film resistance thermometer as a detector of chemi-ionization.

Summary

Acetylene-oxygen reaction in shock waves has been studied over the range of conditions $820° \leq T \leq 1630°K$, $1.8 \leq P \leq 5.6$ atm., $8.4 \times 10^{-4} \leq [O_2] \leq 4.1 \times 10^{-3}$ mol./l. and $0.4 \leq [C_2H_2]/[O_2] \leq 1.5$. Visible emission, OH absorption, and pressure have been measured simultaneously at the same location in the tube. The induction periods obtained from these measurements have been found to be identical with each other and to be dependent upon the oxygen concentration. It has also been found that the activation energy derived from the $\log(\tau[O_2])$ vs. $1/T$ plot is equal to 19.0 ± 0.6 kcal./mol. Thus, the reaction $H + O_2 \rightarrow OH + O$ is considered to be rate-determining during the induction period, as in the hydrogen-oxygen reaction.

The visible emission has been found to have a sharp peak at about 4320Å and has been attributed to the $^2\Delta - ^2\pi$ transition of CH radicals.

The authors are grateful to Mr. Akio Sawa for his help in the experiments and to Mr. Daisuke Miura and Mrs. Yukiko Takemura for their computations of shock parameters.

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