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A Shock-tube Investigation of Ignition in Ethylene-Oxygen-Argon Mixtures

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The ignition of ethylene–oxygen mixtures highly diluted with argon was studied in a shock tube by monitoring the emission from CH* and C_2* or OH*. The measurements covered the temperature range of 1400—2100 K at the C_2H_4/O_2 ratios of 0.33—1.00. From the observation of the CH*, C_2*, and OH* emissions, a mechanism for the production of chemiluminescent species upon ethylene oxidation was briefly discussed, and from the observation of the induction period of the CH* emission, the following equation was found:

$$\log \tau_{CH}[O_2] = -11.45 + 27.5\times10^3/4.58T$$

in units of s mol l^{-1}, the rate-determining step being $C_2H_3+O_2\rightarrow C_2H_3O+O$.

About fifteen years ago, one of the present authors studied the oxidation of ethylene in the temperature range from 700 to 1000 K by the "admission method" and found an apparent activation energy of about 30 kcal/mol.[1)]

Since that time, the shock tube has been adopted as a very important tool for studying ignition processes and the shock-tube oxidation of ethylene has been studied by several investigators, for it allows gases to be heated rapidly and homogeneously so that wall effects and diffusion may be neglected. White[2)] has reported that the induction period of the oxidation depends on both the ethylene and oxygen concentrations at small ratios (0.0025—0.01) of ethylene to oxygen in the temperature range from 1100 to 2200 K, using the interferometrical method. In this case, the total order was about one and the estimated activation energy was 17.3 kcal/mol. Gay *et al.*[3)] have also observed the induction period at higher ratios (0.1—1.5) of C_2H_4/O_2 in the temperature range from 1500 to 2300 K; they found 24 kcal/mol to be the apparent activation energy. On the other hand, by monitoring both the infrared emission from CO and CO_2 and the CH* visible emission, Homer and Kistiakowsky[4)] have obtained the activation energy of 17.1 kcal/mol at C_2H_4/O_2 ratios of 0.17—0.5 in the temperature range from 1500 to 2300 K.

In the present paper, we wish to report the results of simultaneous observations of CH* and C_2* or OH* emissions and wish to interpret the observed emission profiles. Another purpose of this paper is to determine the apparent activation energy of ethylene oxidation by means of measurements with the induction period of the CH* emission in a shock tube.

Experimental

Apparatus and Procedure. The shock tube used in these experiments was composed of a stainless steel tube 4.3 cm in inner diameter. The tube was divided into two sections, that is, the driver section, B (129 cm in length), and the test section, A (250 cm in length), separated by a diaphragm, D_i of polycarbonate or polyester film 25—70 μ thick punctured by a spring-located needle, N. The outline of the apparatus is shown in Fig. 1.

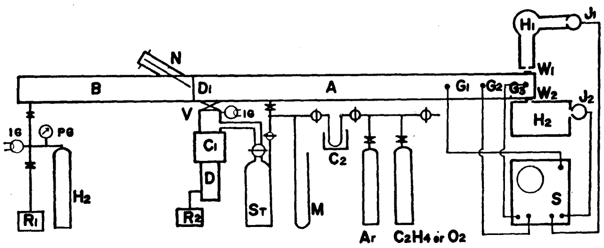

Fig. 1. Schematic diagram of apparatus.

The velocity of the shock waves was measured by using two barium titanate gauges, G_2 and G_3. The G_1 gauge, located at a distance of 210 cm from the diaphragm, D_i, was used for starting the sweep of the synchroscope, S. Both distances, G_1—G_2 and G_2—G_3, were 15 cm. The incident shock speeds were recorded in order to evaluate the reflected shock temperatures.

The quartz windows, W_1 and W_2, located 1 cm from the reflecting plate, could be used to monitor the CH* emission and the C_2* or OH* emission simultaneously during the reaction. At one window, W_1, the measurement of the CH* emission was made using a Hilger prism monochromator, H_1 (with a half-width of 20 Å) equipped with a Hamamatsu R-300 photomultiplier, J_1. At the other window, W_2, the measurement of the OH* or C_2* emission was made using a Rico-MC-20 grating monochromator, H_2 (with a half-width of 25 Å), equipped with a Hamamatsu R-300 photomultiplier, J_2.

The out-put voltages from the gauges (G_2 and G_3) and the photomultipliers (J_1 and J_2) were recorded simultaneously on an Iwatsu DS-5158 A dual-beam synchroscope, S. The time response was better than 1 μs.

The driver section, B, was evacuated until the pressure was about 10^{-3} Torr by means of a rotary pump, R_1, before admitting the driver gas. On the other hand, the test section, A, and the gas sampling system could be evacuated until 1×10^{-5} Torr by the pumping system which included a 2 inch oil-diffusion pump, D, with a liquid nitrogen trap, C_1; the evacuation was checked by means of a cold cathode ionization gauge, IG. The test section, A, of the shock tube was always checked to a pressure of 1×10^{-4} Torr before filling it with a reaction mixture, and the shock was fired within 2 min after isolation from the pumping system, because it has a residual leak at the rate of 2×10^{-4} Torr per minute.

The inner wall of the test section, A, and especially the inner surfaces of the windows (W_1 and W_2) were cleaned after each run with a dry cloth in order to remove any unvolatile products. Also, the reaction mixtures were prepared manometorically and stored in a stainless steel storage vessel, ST (volume, *ca.* 30 l). The line and storage were flushed with argon before the preparation of the mixtures.

The other accessories of this apparatus and the method of operation were similar to those reported in an earlier publication.[5)]

Materials. The ethylene, oxygen, and argon used were obtained from commercial cylinders; the purities were 99.99%, 99.9%, and 99.99% respectively. The driver gas was 99.9% pure-grade hydrogen. All the gases were used without further purification except for passing them through a dry ice trap, C_2.

Samples. The compositions of the reaction mixtures were (1% C_2H_4, 1% O_2, 98% Ar), (1% C_2H_4, 2% O_2, 97% Ar), and (1% C_2H_4, 3% O_2, 96% Ar), and the initial pressures of the reaction mixtures used were about 50 Torr and 100 Torr. Each shock-run was denoted a or b for the initial pressures of 50 Torr and 100 Torr, and 1, 2, and 3 for the oxygen concentrations of 1%, 2%, and 3% respectively. For example, 3a corresponds to the initial pressure of 50 Torr and the oxygen concentration of 3%.

Results and Discussion

The reflected shock temperatures were calculated from the measured incident shock velocities, using the three conservation equations and the ideal equation of a state assuming a thermal equilibrium.

Interpretation of Observed Emission Profiles. In the present experiments, we observed the C_2* emission at 5165 Å, the CH* emission at 4515 Å, and the OH* emission at 3067 Å. The CH* emission intensity observed using a Rico-MC-20 grating monochromator was about 1.4 times that observed using a Hilger prism monochromator at 4315 Å. In addition, the Hamamatsu R-300 photomultiplier has a different response of intensity according to the wavelength, that is, it is 100 at 3067 Å, 85 at 4315 Å, and 52 at 5165 Å. These values were applied in order to correct the emission intensities which were directly obtained from the observed emission profiles, as is shown in Fig. 2.

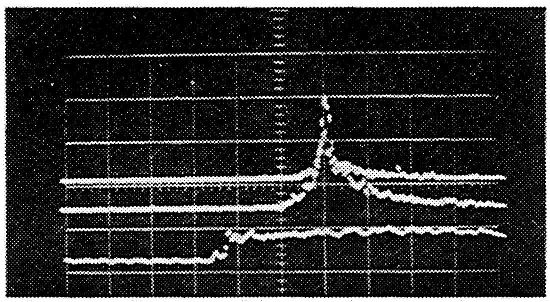

Fig. 2. Comparison of time history of CH* emission using the prism monochromator and OH* emission using the grating monochromator,
$T_5 = 1506$ K, $P_5 = 1495$ Torr, sweep=50 μs/div..
Upper trace: OH* emission at 3067 Å using grating monochromator, gain=0.05 V/div.
Middle trace: CH* emission at 4315 Å using the prism monochromator, gain=0.1 V/div.
Lower trace: G_3 signal.

The following characteristics were obtained from the emission profiles of each run:

1. The maximum emission intensity of OH* was considerably smaller than those of CH* and C_2*, showing a ratio of emission intensity of about 10 (CH*): 10 (C_2*): 1 (OH*); it was not distinguishable from noises, especially in the range of lean oxygen.

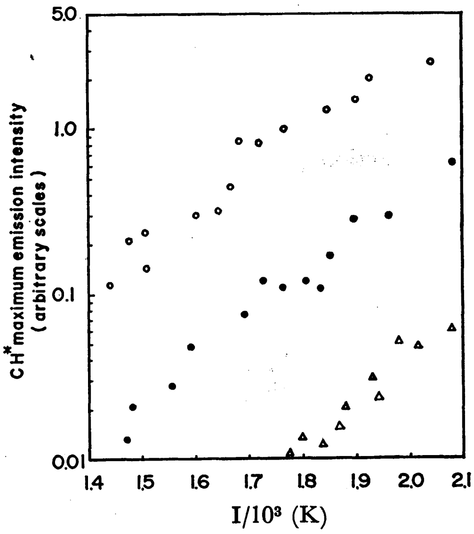

Fig. 3. Comparison of CH* maximum emission intensity of series a at various temperatures.

2. The maximum intensity of the CH* emission decreased extremely at both a lowering of the temperature and a decrease in the O_2 concentration, as is shown in Fig. 3; the OH* emission showed similar behavior.
3. The maximum intensity of the C_2* emission shows no clear dependence on the O_2 concentration, unlike the CH* and OH* emissions.
4. The onset of emission was qualitatively observed to be in the order of: CH*, C_2*, and OH*.

Several reaction mechanisms have been proposed by Gaydon[6)] and Hand and Kistiakowsky[7)] for the formation of CH* in hydrocarbon flames, *e.g.*;

$$C_2 + OH \longrightarrow CH^* + CO \qquad (1\text{-}1)$$

$$C_2H + O_2 \longrightarrow CH^* + CO_2 \qquad (1\text{-}2)$$

$$C_2H + O \longrightarrow CH^* + CO \qquad (1\text{-}2')$$

The present experimental results indicate that the CH* emission arises mainly from Reactions (1-2) and (1-2′) rather than from (1-1), because of the great dependence of the O_2 concentration on the CH* emission; the onset of emission was observed in the order of: CH*, C_2*, and OH*.

Secondly, as to the production of C_2* in hydrocarbon flames, several reactions have been considered by Ferguson,[8)] Miller and Palmer,[9)] and Gaydon and Wolfhord,[10)] *e.g.*;

$$CH + CH \longrightarrow C_2^* + H_2 \qquad (1\text{-}3)$$

$$C + CH \longrightarrow C_2^* + H \qquad (1\text{-}4)$$

$$CH_2 + C \longrightarrow C_2^* + H_2 \qquad (1\text{-}5)$$

$$C_2O + C \longrightarrow C_2^* + CO \qquad (1\text{-}6)$$

As CH_2 and C_2O may not be produced during C_2H_4 oxidation, the C_2* emission may arise from (1-3) and (1-4).

The production of OH* in hydrocarbon flames has been explained by this reaction:

$$CH + O_2 \longrightarrow CO + OH^* \qquad (1\text{-}7)$$

for which evidence has been reported.[6,11)]

The intensity of OH* emission was greatly dependent on the O_2 concentration, just like the CH* emission, and the intensity of the OH* emission was weak as compared with the intensities of CH* and C_2*. This implied that OH* emission may arise from Reaction (1-7); thus, Reaction (1-3) or (1-4) and Reaction (1-7) should be competitive reactions which consume the ground-state CH, while Reaction (1-2) or (1-2′) and Reaction (1-7) are also competitive reactions which consume oxygen.

It seemed that it would be very interesting to know exactly the process of the onset of emission in order to discuss the reaction mechanism. The order of the onset of emission was, qualitatively, the CH*, C_2*, and OH* emissions, as has been described above. However, we cannot discuss the reaction mechanism in detail on the basis of the CH*, C_2*, and OH* order of emission onset because of the complexity of the phenomena of the CH*, C_2*, and OH* emissions.

Induction Period. Table 1 summarizes the experimental conditions of the four groups of runs and the results of the measurement of the induction period, τ_{CH}, which is defined as the time lag between the reflected shock arrival and the onset of the CH*-emission signal. Figure 4 shows the plot of log τ_{CH} *versus* 1/T for three experimental groups, 3a, 2a, and 1a. It can readily be seen that the values of log τ_{CH} in Groups 3a, 2a, and 1a fall on a single linear line, indicating the effect of oxygen on the induction period. Figure 5 shows the plotting of log $\tau_{CH}[O_2]$ *versus* 1/T for four groups of experiments, 3a, 2a, and 1a, and 1b; all the points fit a single line. The temperature coefficient of the induction period can be obtained from the slope of the line drawn in Fig. 5. Consequently, over the temperature and concentration ranges covered by the present experiments, the induction period for the

TABLE 1. EXPERIMENTAL CONDITIONS AND INDUCTION PERIODS

Series	Shock No.	T_5 K	P_1 Torr	P_5 Torr	τ_{CH}* μs
3a	3001	1443	50.1	1386	93
	3004	1677	50.6	1760	30
	3005	1600	50.4	1633	35
	3006	1645	49.8	1684	30
	3007	1633	50.3	1682	36
	3008	1508	50.2	1486	68
	3009	1506	50.6	1495	63
	3010	1474	50.7	1450	79
	3013	1508	50.3	1489	80
	3014	1811	49.7	1938	14
	3016	1664	51.0	1752	26
	3018	1582	50.1	1596	49
	3019	1597	47.0	1518	41
	3020	1459	50.2	1412	108
	3021	1575	50.1	1561	45
	3022	1534	50.9	1547	68
	3024	1422	49.8	1347	108
	3027	1720	50.9	1839	19
	3029	1735	50.1	1834	24
	3030	2042	51.3	2374	6
	3031	1844	50.1	2005	10
	3032	1924	49.8	2118	8
	3034	1766	50.2	1886	15
	3035	1806	50.2	1947	16
	3036	1675	50.1	1739	22
	3038	1841	50.5	2016	12
	3039	1716	51.1	1840	22
	3040	1897	50.8	2120	10
2a	2002	1830	51.3	2018	20
	2003	1733	49.8	1809	27
	2005	1729	50.0	1811	28
	2006	1852	50.0	2001	15
	2007	1765	49.8	1858	31
	2009	1693	50.5	1771	40
	2011	1804	49.6	1970	25
	2012	1756	50.0	1851	37
	2015	1797	51.6	1975	22
	2016	1723	50.1	1803	36
	2017	1827	49.6	1945	23
2a	2020	1898	50.0	2074	19
	2022	1960	50.8	2206	15
	2024	1469	49.9	1411	152
	2025	1588	50.8	1618	74
	2027	1937	50.0	2135	15
	2028	1924	50.4	2237	14
	2030	1726	50.1	1809	35
	2031	1799	50.6	1941	27
	2033	1480	50.3	1440	150
	2035	2081	50.2	2372	8
	2036	1555	50.3	1553	77
	2038	1847	50.3	2005	16
1a	1001	1774	50.0	1841	53
	1002	1786	50.0	1890	44
	1004	1981	50.4	2213	22
	1006	1786	50.2	1894	42
	1007	1868	50.5	2039	32
	1008	1860	50.8	2038	28
	1010	1809	51.1	1957	38
	1011	1929	50.7	2144	21
	1013	1779	51.1	1921	44
	1014	1769	51.1	1904	41
	1015	1880	50.0	2038	25
	1016	2007	50.2	2245	16
	1018	1939	51.8	2207	18
	1020	2009	50.3	2254	18
	1021	1837	50.2	1979	36
	1022	2077	49.1	2304	13
	1023	1804	50.6	1941	42
1b	1125	1716	100.0	3566	34
	1126	1629	101.3	3344	49
	1127	1751	100.6	3693	28
	1129	1846	93.8	3721	18
	1130	1679	101.6	3507	50
	1131	1596	100.0	3202	55
	1133	1694	101.2	3538	44
	1134	1797	99.6	3803	23
	1135	1634	101.1	3350	62

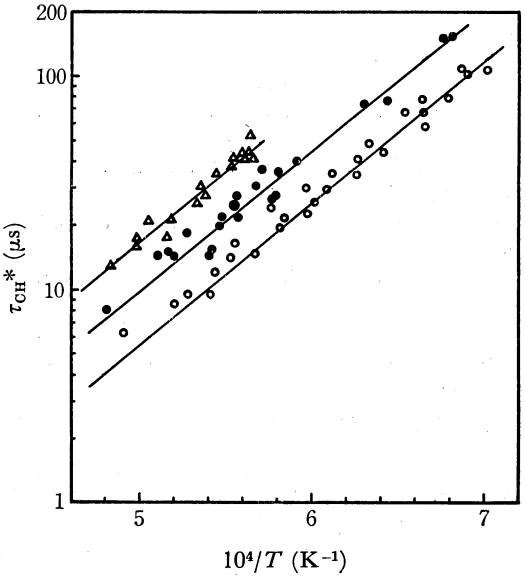

Fig. 4. A plot of log τ_{CH}* *versus* $1/T$ for three reaction mixtures at initial pressure of about 50 Torr.
○: 3% O_2+1% C_2H_4, ●: 2% O_2+1% C_2H_4,
△: 1% O_2+1% C_2H_4.

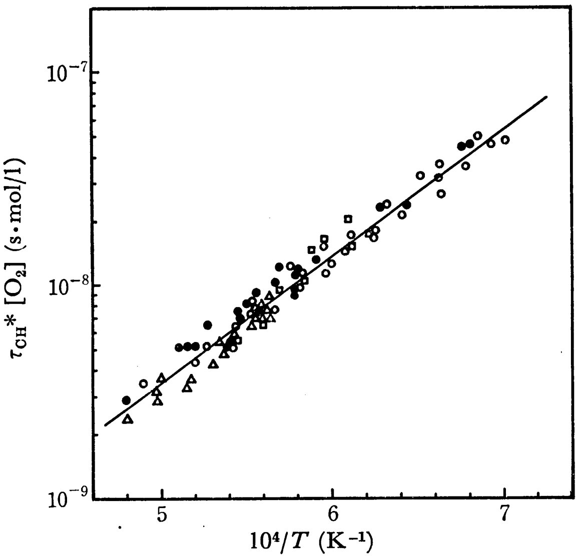

Fig. 5. A plot of log τ_{CH}*[O_2] *versus* $1/T$ for three reaction mixtures.
Initial pressure of about 50 Torr,
○: 3% O_2+1% C_2H_4, ●: 2% O_2+1% C_2H_4,
△: 1% O_2+1% C_2H_4.
Initial pressure of about 100 Torr,
□: 1% O_2+1% C_2H_4.

CH* emission can be represented as:

$$\log \tau_{CH}[O_2] = -11.45 + 27.5 \times 10^3/4.58T$$

in units of s mol l^{-1}.

White,²⁾ examining very lean mixtures (fuel/oxygen—0.1), observed that the induction periods before any detectable heat release from the C_2H_4–O_2 and C_2H_2–O_2 reactions were similar to each other in the temperature range from 1100 to 2200 K and led to an essentially common activation energy of 17.3 kcal/mol. Gay *et al.*,³⁾ using C_2H_4/O_2 ratios of 0.1—1.5, reported that the induction period and the intensity of chemiluminescence from CH* were similar in magnitude to those found in the C_2H_2–O_2 reaction, especially at the higher temperatures of 1800—2100 K. At lower temperatures, towards 1500 K, the induction periods were significantly greater than in the case of C_2H_2; the results gave an activation energy 24 kcal/mol larger than the 17 kcal/mol found for C_2H_2–O_2. They detected quite large concentrations of acetylene during the course of the C_2H_4–O_2 reaction and proposed the following tentative schemes:

	ΔH (kcal/mol)	
$C_2H_3 + O_2 \longrightarrow C_2H_3O + O$	+27	(2-1)
$O + C_2H_4 \longrightarrow C_2H_3 + OH$	+3	(2-2)
$OH + C_2H_4 \longrightarrow C_2H_3 + H_2O$	−14	(2-3)
$C_2H_3 + O_2 \longrightarrow 2CO + H_2 + H$	−67	(2-4)
$C_2H_3 + O_2 \longrightarrow C_2H_2 + HO_2$	+5	(2-5)
$C_2H_3O + M \longrightarrow C_2H_2 + OH + M$	+30	(2-6)
$C_2H_3O + O_2 \longrightarrow 2CO + H_2O + H$	−100	(2-7)
$C_2H_3 + M \longrightarrow C_2H_2 + H + M$	+41	(2-8)
$H + C_2H_4 \longrightarrow C_2H_3 + H_2$	+1	(2-9)

To satisfy the higher activation energy, they suggested that the rate-determining step was (2-1), the endothermicity being 27 kcal/mol.

On the other hand, Homer and Kistiakowsky⁴⁾ reported an activation energy of 17 kcal/mol and the rate-determining step of:

$$H + O_2 \longrightarrow OH + O \qquad (2\text{-}10)$$

at lower ratios of C_2H_4/O_2. They then proposed that the C_2H_4–O_2 reaction, in its early stages, consists mainly of the pyrolysis to the C_2H_2 and H_2 above 1800 K. They have also suggested the existence of some value larger than 24 kcal/mol controlling the ethylene-oxidation mechanism involving such intermediates as have been postulated by Gay *et al.*

The measurement of the induction period in the shock tube has been undertaken in the hope that it would offer a convenient method elucidating an activation energy and would be able to suggest a rate-determining step. The value of the apparent activation energy obtained from the present experiment is 27.5 kcal/mol at 1400—2100 K, the value of Gay *et al.* is 24 kcal/mol at 1500—2300 K, and our previous work¹⁾ has shown the value of 30 kcal/mol in the range of 700—1000 K in spite of the difference in method. The variation in the apparent activation energy with the temperature has also been considered.¹²⁾ Since a rate-determining step in an elementary reaction will vary with the temperature and the composition, the difference in these values can be understood. As has been mentioned above, White and Homer *et al.* have reported an activation energy of about 17 kcal/mol at lower ratios of C_2H_4/O_2, and Gay *et al.* have reported an activation energy of 24 kcal/mol at higher ratios of C_2H_4/O_2. The value of activation obtained from the present experiment at higher ratios of C_2H_4/O_2 is 27.5 kcal/mol. Hence, it seems that, in the C_2H_4 oxidation, Reaction (2-10) is predominant at lower ratios of C_2H_4/O_2 and

Reaction (2-1) is predominant at higher ratios of C_2H_4/O_2. Considering the schemes proposed by Gay *et al.*, it may be supposed that the reaction:

$$C_2H_3 + O_2 \longrightarrow C_2H_3O + O \qquad (2\text{-}1)$$

is the rate-determining step for ethylene oxidation under our experimental conditions. Since Reaction (2-1) is endothermic, the activation energy of Reaction (2-1) should be larger than its endothermicity (27 kcal/mol).13) The apparent activation energy obtained, 27.5 kcal/mol, satisfies the above relation. Therefore, the apparent activation energy, 27.5 kcal/mol, obtained from our measurements seems reasonable.

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