Acetylene Detonations near the Upper Limit of Detonability

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In the past detonations in the acetylene oxygen system have often been investigated in tubes, which were relatively short compared to their diameter. This paper describes experiments with detonations and combustion processes for acetylene concentration from 50 to 100 % in tubes of 10, 16 and 24 mm diameter and tube length corresponding to 1000 tube diameters or more. Initial conditions were room temperature and normal pressure. The detonations were photographed with a drum camera over a tube length of 2 m. In addition pressure profiles were registered at different positions. For the initiation of the detonations fully developed "good" detonations of mixtures of C_2H_2/O_2 were used. The measured detonation velocities [1] were in good agreement with those reported by Dixon, Breton [2], Le Chatelier, Kistiakowsky [3, 4] a. o. Up to the limit of soot formation ($\approx$ 55 % C_2H_2) they were also in good agreement with calculated (ZND model) values.

For richer mixtures, towards the upper limits of detonability the velocity fluctuations of the detonations increased. This can be attributed to a large extent to the formation of soot and it is as well observed in detonations of other fuel-oxidizer systems which form soot [5, 6, 7].

The limits of detonability (see Fig. 1) reported by Breton [2] and by Kistiakowsky [3] are at 92, resp. 90 % C_2H_2. They have been measured in relatively short tubes. In our experiments we found similar values in the 10 and 16 mm tubes for a tube length of 4 m. For longer tubes (> 9.5 m) the limit of detonability came close to 95 %. Towards the limit velocity fluctuations become, however, rather large as shown in Fig. 1. The line 2 in Fig. 1 are computed values from Kistiakowsky for gaseous reaction products, line 3 includes heterogeneous (graphite) products. Line 5 is computed for soot with a hydrogen content of 7 mole % as found in our experiments. As photographs show, the deviation between measured and computed detonation velocities are related to the extension of the soot formation zone.

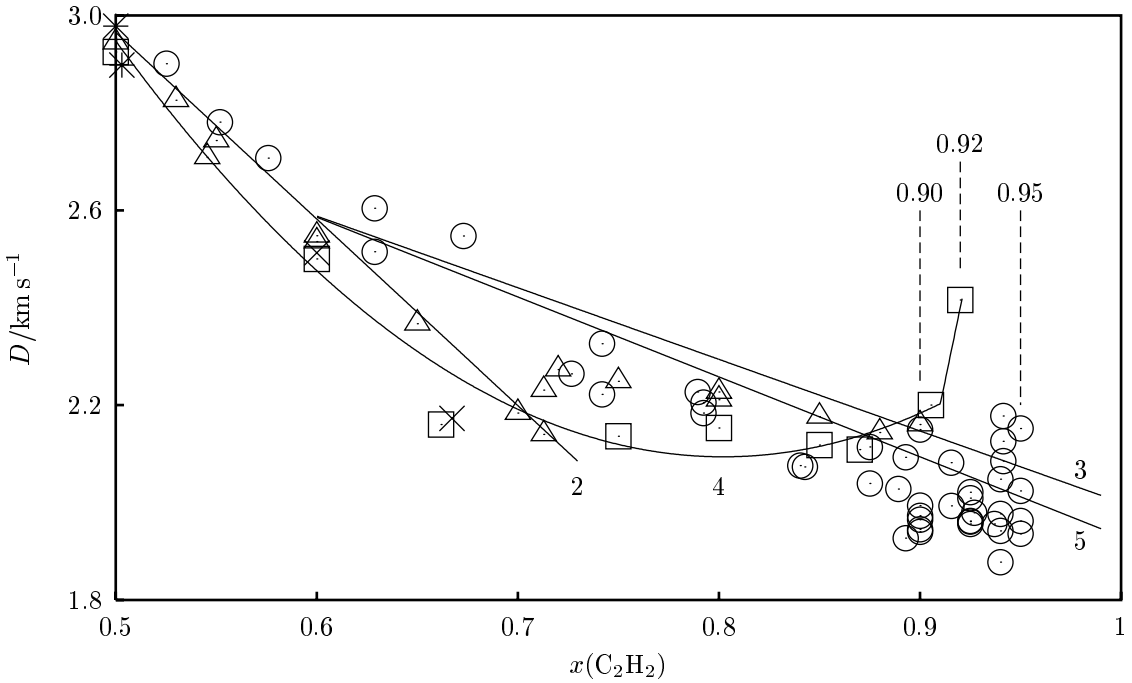
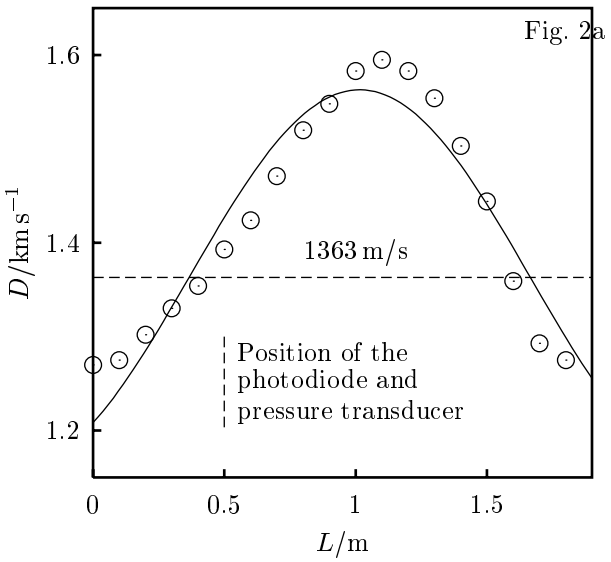
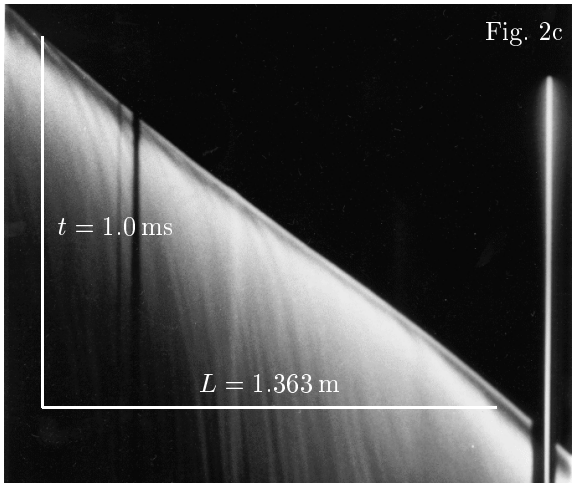


Figure 1: Experimental detonation velocities as a function of the acetylene fraction. □ Breton △ Kistiakowsky ∗ Dixon × Le Chatelier ○ this work. The dashed lines indicate the limits of detonability. Line 2 and 3 show the computed velocities of Kistiakowsky for homogeneous and heterogenous equilibrium, line 4 is a best fit for Breton's data and line 5 show the computed data for this work.





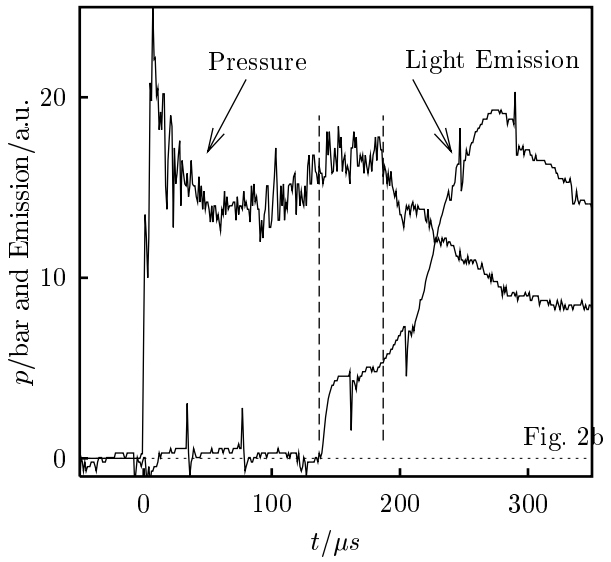


Figure 2: Pyrolysis of 100% acetylene. $T = 19°C$, $p = 748.2$ Torr, $d_{\mathrm{tube}} = 24$ mm, $l_{\mathrm{tube}} \approx 1000 \cdot d_{\mathrm{tube}}$. a) Flame velocity D as function of distance L. b) Pressure and light emission profile taken at $L = 0.5$ m. The position of the first and second flame front are indicated by dashed lines. c) Drum camera picture.

The detonations observed in 10, 16 and 24 mm tubes show up to about 90 % C_2H_2 single headed spin with the usual ratio of spin-wavelength L_S to tube diameter d_{ar}. For increasing C_2H_2 concentration this ratio increases slightly but systematically and the "flame front" shows a regular pulsation with increasing amplitude towards the limit which repeats after roughly 15 spin wavelength. Near and outside the upper limit of detonability different interesting structures can be observed [8, 9, 10] which appear clearly in pure acetylene. This is shown by the following example: A process in 100 % C_2H_2 propagating in a 24 mm diameter tube is show in Fig. 2. The flame front for 100 % C_2H_2 (24 mm diameter tube diameter) propagates with a nearly sinusoidal velocity profile (Fig. 2a). It is formed by two yellow luminous zones which follow the shock front at a distance of 130 and 190 μs (see Fig. 2b) and which are positioned at the two sides of a secondary pressure wave. Between the two yellow luminous zones a red luminosity can be registered on a color film. Figure 2c shows a photo of that process. The pressure and light intensity measurements in Fig. 2b have been taken at a position where the "flame velocity" has the mean value of 1360 m/s.

With increasing local flame velocity, the distance between the two yellow luminous zones decreases and the light intensity and the amplitude of the secondary pressure wave increase. This is an indication for the interaction between the front shock wave and the secondary pressure wave, resp. the soot formation process. For these processes called here "pyrolysis flames" an important regular transversal structure could not be observed on the films and from the pressure records.

Measurements as shown in Fig. 2 have been performed for many different conditions. The stability of these "pyrolysis flames" in very rich C_2H_2/O_2 mixtures or in C_2H_2 proved to be quite good and they could be observed propagating after distance of more than one or two thousand tube diameters. There

seems to be a critical tube diameter for pyrolysis flame in pure C_2H_2. In a 10 mm diameter tube pyrolysis flames in pure C_2H_2 did not propagate over a longer distance but they can be observed in connection with the pulsating detonations which are also observed above and near the limit of detonability. Characteristic differences of the pyrolysis flames are also observed when small amounts of inert gas are added to the acetylene. In addition there seems to be a critical initial pressure. In a 24 mm tube pyrolysis flames in pure C_2H_2 did not propagate over large distances at pressure below 735 Torr.

The temperature behind the shock front T_N of the "C_2H_2-pyrolysis flames" computed for a one dimensional shock front are rather low ($T_N \approx 900$ K). This requires indeed long induction times for the reactions [11, 12, 13, 14, 15, 16, 17] in the C_2H_2 systems even at the high carbon atom concentrations used here. In addition the time for the heat transfer to the gas from the many formed small soot particles may become rather long, so that only part of the reaction enthalpy will be available for the propagation of the "pyrolysis flame". For a detailed description of that process, the model of Borisov and co-workers [18, 19] can be used.

The pyrolysis flames will be discussed in relation with soot formation experiments in different hydrocarbons and compared with corresponding results obtained by Tesner et al. [17] at higher initial pressures.

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