

Opposite influence of haloalkanes on combustion and pyrolysis of acetylene

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Abstract. An influence of haloalkanes CF_3H and CCl_4 (known as inflammation and explosion suppressors) on combustion and pyrolysis of acetylene behind shock waves was experimentally studied. While ignition delay times in stoichiometric acetylene-oxygen mixtures were expectedly increased by halogenoalkanes admixtures, the induction times of carbon particle formation at acetylene pyrolysis were dramatically reduced in presence of CCl_4 . A simplified kinetic model was suggested and characteristic rates of diacetylene C_4H_2 formation were estimated as a limiting stage of acetylene polymerization. An analysis of obtained data has indicated that promoting species is atomic chlorine forming in CCl_4 pyrolysis, which interacts with acetylene and produces C_2H radical, initiating a chain mechanism of acetylene decomposition. The results of kinetic modeling agree well with experimental data.

1. Introduction

Various haloalkanes have a long history of their practical use in firefighting. It is commonly supposed that their efficiency of combustion suppression originates not only from oxygen replacement and the significant endothermicity of their vaporization and pyrolysis, which rapidly drops the temperature of the mixture, but also from the chemical inhibition of the chain reactions of combustion. The basic of chemical inhibition mechanism was presented in [1]. Nevertheless, in that classic work a counter promoting influence of chlorinated species on ignition at particular conditions was already mentioned. In a number of recent works it was shown that halogenated hydrocarbons considered as flame inhibitors may as well accelerate ignition [1–5] and even be combustible themselves [6]. An influence haloalkanes on combustion processes is still an actual scientific task of a great importance for modern fire extinguishing systems development and industrial risks analysis. Therefore, the experimental study of ignition of haloalkane-containing mixtures in a wide range a elaboration of a comprehensive model of pyrolysis and oxidation of haloalkanes and their influence of combustion is quite topical.

Important feature of acetylene is its ability to self-pyrolysis and detonation without oxidizer. In recent works [7, 8] it was shown that unlike a usual detonation, such wave is supported by energy of condensation of supersaturated carbon vapor, i.e., it is a detonation wave of condensation. Thus even small additives of oxygen lead to combustion of part of acetylene and change of all subsequent kinetics of pyrolysis and condensation. Thus, investigation of ignition carbon particle formation in super-rich acetylene–oxygen mixtures (fuel-oxygen ratio up to 10-30)



is quite actual. Particularly, the influence of halogenated species on the acetylene self-pyrolysis and detonation (which can happen spontaneously without an oxidant [6] and significantly complicates technologies of acetylene production and storage) remains barely investigated.

This work was devoted to investigation of influence of fluoroform CF_3H (Freon-23) and carbon tetrachloride CCl_4 (Halon-104) admixtures on acetylene combustion and pyrolysis.

2. Experimental methods

Experiments were performed behind the reflected shock waves in a stainless steel shock tube of a conventional design with inner diameter of 50 mm. Lengths of high- and low-pressure section were 1.5 and 3.0 m correspondingly. Shock tube was equipped with several piezoelectric gauges (including one, installed at the end plate) which allow measuring incident shock wave velocity with an accuracy $\approx 0.5\%$ and the calculation parameters of shock-heated media behind the reflected wave using common iteration method [9]. Investigating cross-section where the optical diagnostics were placed was located at the distance 13 mm from the end plate of the tube. The investigated gas mixtures were prepared manometrically. Reference values of induction times were measured in the mixtures $3.5\text{--}20\%(2\text{C}_2\text{H}_2+5\text{O}_2)+\text{Ar}$ and $10\text{--}30\%\text{C}_2\text{H}_2+\text{Ar}$. An influence of halogenated admixtures on acetylene combustion was investigated in the mixtures $3\%\text{CF}_3\text{H}/\text{CCl}_4+20\%(2\text{C}_2\text{H}_2+5\text{O}_2)+\text{Ar}$, $2\%\text{CF}_3\text{H}/\text{CCl}_4+10\%(2\text{C}_2\text{H}_2+5\text{O}_2)+\text{Ar}$ and $0.5\%\text{CF}_3\text{H}/\text{CCl}_4+3.5\%(2\text{C}_2\text{H}_2+5\text{O}_2)+\text{Ar}$. Experiments devoted to investigation of halogenoalkanes on acetylene pyrolysis and carbon particle formation were carried out in mixtures $3\%\text{CF}_3\text{H}/\text{CCl}_4 + 30\%\text{C}_2\text{H}_2 + \text{Ar}$ and $3\%\text{CCl}_4+10\%\text{C}_2\text{H}_2+\text{Ar}$. Besides that the processes of ignition and carbon particle formation in super-rich mixtures $10\%\text{C}_2\text{H}_2+1\%\text{O}_2+\text{Ar}$, $10\%\text{C}_2\text{H}_2+3\%\text{O}_2+\text{Ar}$ and $3\%\text{CCl}_4+10\%\text{C}_2\text{H}_2+3\%\text{O}_2+\text{Ar}$ were also studied.

Radical OH is the characteristic species for hydrocarbons combustion. During the experiments in acetylene–oxygen mixtures an OH emission signal registered by the photomultiplier equipped with interference filter 310 ± 5 nm was used for the determination of ignition delay times in all investigated mixtures. Moment of the rapid rise of OH emission was considered as ignition moment (technically, the exact ignition moment was determined as the intersection of the inflectional tangent line of the OH radiation record with the time axis). Simultaneously an increase of pressure was registered by pressure gauge in the same section of shock tube. Typical experimental signals of pressure and OH emission are presented in Fig 1.

Registration of laser extinction signal (usually by He-Ne laser at wavelength 632 nm) is a common diagnostic method of particle formation in gaseous media. In figure 2 typical pressure and extinction profiles measured during shock wave propagation in mixture $30\%\text{C}_2\text{H}_2+\text{Ar}$ are presented. Two schlieren-peaks on extinction signal correspond to the fronts of incident and reflected shock wave (ISW and RSW) propagation. One can see that similarly to ignition process, the intensive formation of condensed particles occurs after some induction time (about $150\text{ }\mu\text{s}$), during which the pressure corresponds to calculated P_5 value. Then, a fast heat release during the condensation leads to significant pressure rise. In present work the pilot temperature measurements during the reaction time were performed by the generalized line reversal method on the sodium D-line at 589 nm. This method is based on simultaneous detection of emission and absorption of reactive mixture at the same wavelength. The main advantage of this method is that it requires only a calibrated light source; no knowledge of either optical properties of observable reaction mixture nor of the spectral sensitivity of the detection system is needed. Sodium atoms are the inherent natural impurity in argon and generally they should be in the thermal equilibrium with the integral temperature of the mixture. The measurements were carried out by two identical optical channels that focus the light from the probe region via the pair of the calcium fluoride windows installed in a horizontal plane of the shock tube and further via lenses onto two photomultipliers (figure 3). The first channel registered an emission only. The second channel was exposed to radiation from reference source of known brightness

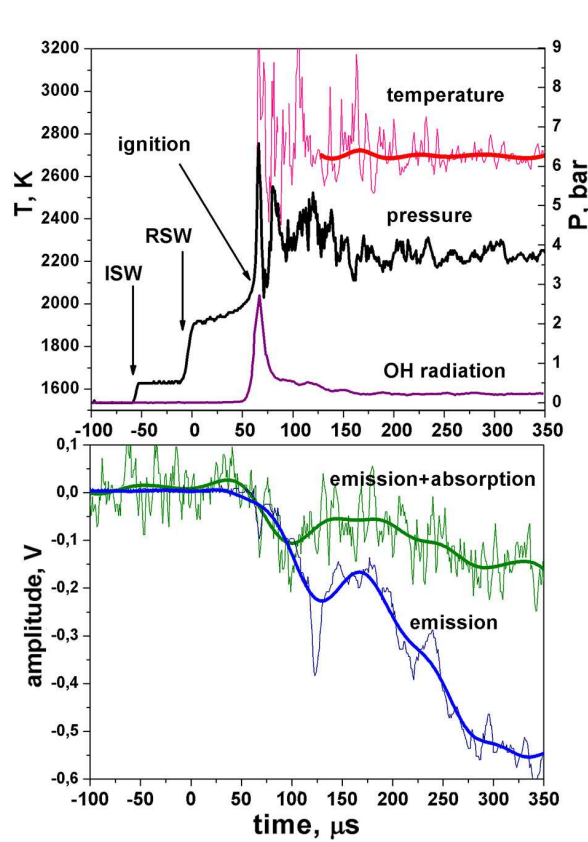


Figure 1. Typical signals obtained in mixture 15%(2C₂H₂+5O₂)+Ar. T₅=1190 K, P₅=2.15 bar.

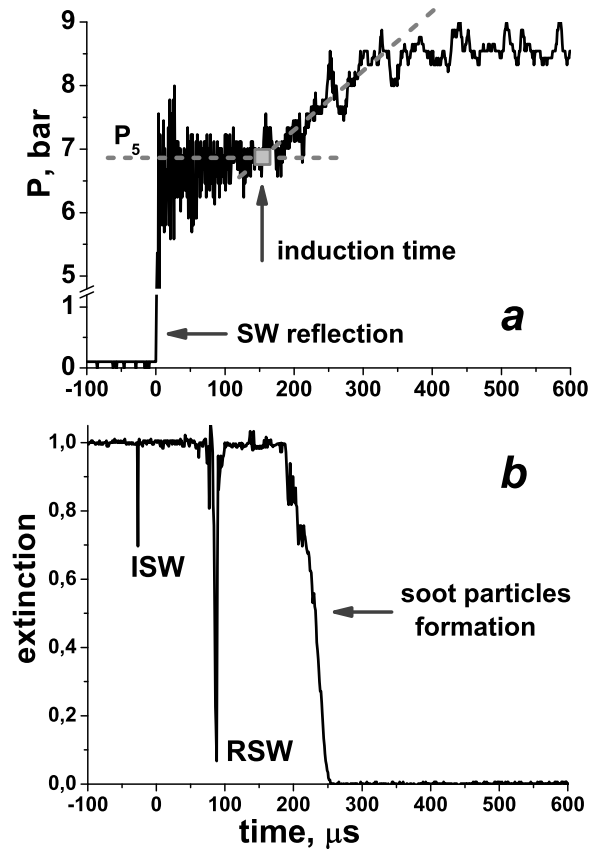


Figure 2. Typical profiles of pressure (a) and extinction (b) obtained in mixture 30%C₂H₂+Ar. T₅=1570 K, P₅=6.3 bar.

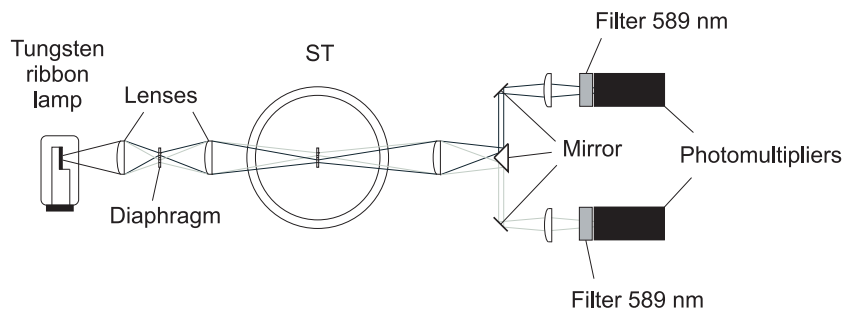


Figure 3. The scheme of emission-absorption spectroscopy diagnostic.

temperature. Thus the second channel detected the combination of absorption and emission of reaction mixture. A calibrated etalon tungsten ribbon lamp was used as a reference light source. The light from the tungsten lamp was collimated with a lens and forwarded through the probe volume. The time resolution of the detection system was about 10 μs, the space resolution was 3 mm.

Taking into account Lambert-Beer's and Kirchhoff's laws one can get the expression for the temperature determination [10]:

$$T(t) = \frac{hc}{\lambda k_B} \left(\ln \left[1 + \left(\exp \left(\frac{hc}{\lambda k T_0} \right) - 1 \right) \left(1 - \frac{I_a(t) - I_0}{I_e(t)} \right) \right] \right)^{-1}. \quad (1)$$

Here h is the Plank constant; c —the speed of light; λ —the diagnostic wavelength; k_B —the Boltzmann constant; T_0 —the brightness temperature of reference source; I_a , I_e , I_0 —the intensities of emission+absorption signal, emission signal and the incoming intensity of radiation of the reference source correspondingly. Typical emission and emission+absorption signals and the temperature profile obtained during their analysis are presented in Fig 1.

Temperature measurements provide additional integral parameters and are valuable for kinetic mechanism elaboration and verification of numerical models.

3. Results and discussion

3.1. Acetylene ignition

The values of ignition delay time registered in stoichiometric acetylene–oxygen mixtures doped with halogenoalkanes are presented in figure 4. One can see that expectable inhibiting influence of studied admixtures was observed. Ignition times in acetylene were just slightly increased in presence of CF_3H admixture and addition of CCl_4 had considerably shifted temperature dependence of ignition time to higher temperatures. Obviously, the observed inhibition is the case of general combustion suppression mechanism [1] suggesting that generalized halogenated species X participates in the following reactions:



where R is a radical, less active than H and/or O . These reactions are in concurrence with the chain reactions that determine combustion progress:



Detailed description of the inhibition kinetic, though, is quite difficult due to high complexity of haloalkanes pyrolysis and oxidation mechanisms involving numerous active species. Thus, the kinetics of radical consumption barely can be reduced to several key reactions while thorough design of corresponding mechanism was out of frame of this work. Since commonly used *GRI-Mech 3.0* kinetic mechanism including acetylene-related reactions is declared to be unsuitable for modeling of pure acetylene combustion, a comprehensive kinetic scheme of acetylene oxidation provided in [11] was used during analysis. Kinetic modeling was performed using the ChemKin software package [12] under isobaric conditions. Calculated values of ignition delay times are shown in figure 4 as lines. One can see, that there is good agreement between experimental and modeling results for 3.5%($\text{C}_2\text{H}_2 + 2.5\text{O}_2$)+Ar mixture, but for less diluted mixtures measured induction times occur to be much shorter than predicted ones.

It's notable that among the data reviewed in [11] there is a work [13] where authors reported ignition delay times which also were not satisfactorily described by suggested kinetic mechanism and were much shorter than ones predicted by general heuristic dependence of ignition delay time (measured in microseconds) on temperature and mixture components concentrations:

$$\tau = 10^{-7.035} \exp\left(\frac{9770}{T}\right) [\text{C}_2\text{H}_2]^{-0.236} [\text{O}_2]^{-0.701} [\text{Ar}]^{0.015}. \quad (8)$$

Authors of [11] suggest that such results were caused by impurity, but one should note that it is the only one of 9 sources and 20 datasets providing data in 950–1200 K region and the study

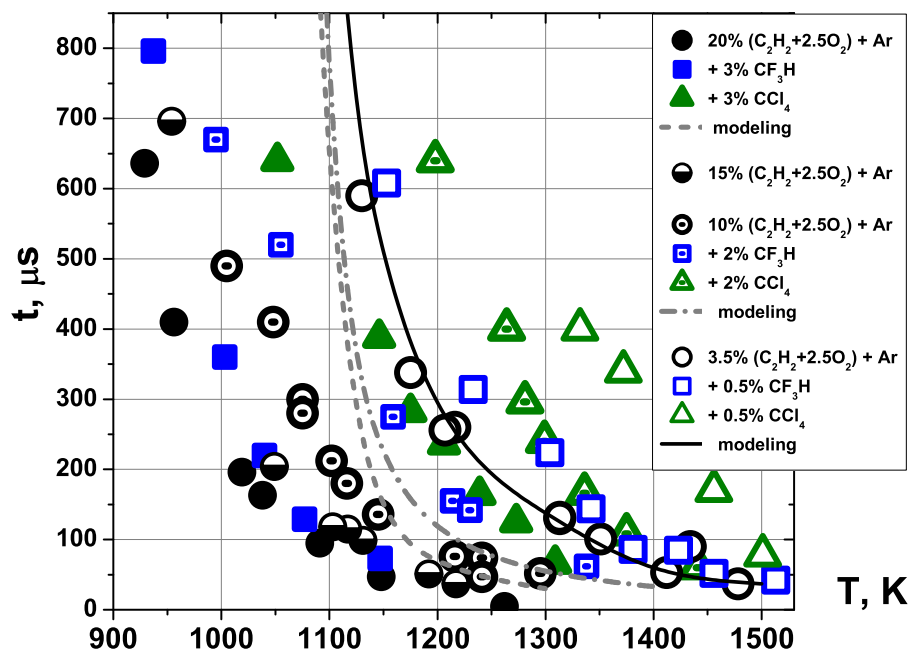


Figure 4. Experimental (dots) and modeled (lines) temperature dependencies of ignition delay times in acetylene–oxygen mixtures doped with haloalkanes at pressures 2.0–2.6 bar.

was performed behind the reflected shock waves in moderately diluted $10.8\% \text{C}_2\text{H}_2 + 8.5\% \text{O}_2 + \text{Ar}$ mixture, while in all other cited works C_2H_2 concentration did not exceeds 3.0%. Notable that 20%-diluted hydrogen-oxygen and methane-oxygen stoichiometric mixtures studied earlier at the same conditions seems to be not strongly affected by such flaws in spite of comparable energy release. Thus, we cautiously conclude that obtained results indicate actual kinetic features of C_2H_2 oxidation, decomposition and polymerization leading to ignition accelerating. An indirect evidence of such kinetic processes is the considerable pressure rise during the induction time (see figure1) registered in acetylene–oxygen mixtures only, while inert gases and hydrogen- and methane-oxygen mixtures of same dilution demonstrates just the very minor pressure rise behind the reflected wave which is the common feature of a shock tube.

3.2. Acetylene pyrolysis and condensation

During the analysis of results of experiments carried out in argon-diluted acetylene the values of induction times at various pressures and C_2H_2 concentrations were normalised to carbon concentration $[\text{C}]$ in the investigated mixtures. As it was shown recently [7, 8], such normalisation allows comparison the results obtained in quite a wide range of C_2H_2 concentrations (0.2–10%) and mixture pressures (1–30 bar). The obtained results for $\tau \cdot [\text{C}] = f(T)$ are presented in figure 5. On the same plot the averaged temperature dependence of induction time of particle formation in acetylene pyrolysis, extracted from data [8], is shown. One can see that induction times in the mixture containing CF_3H are quite close to those observed in acetylene-argon mixtures without halogenated additives. The CCl_4 admixture, in contrast, dramatically reduced the induction times of particle formation.

To get a qualitative idea about the reasons for the observed influence of halogenated hydrocarbons on the promotion of particle formation at acetylene pyrolysis, the simplified kinetic scheme of the first stages of the reaction was considered. A detailed description of the entire process of the pyrolysis of acetylene including the condensed particle formation is quite difficult

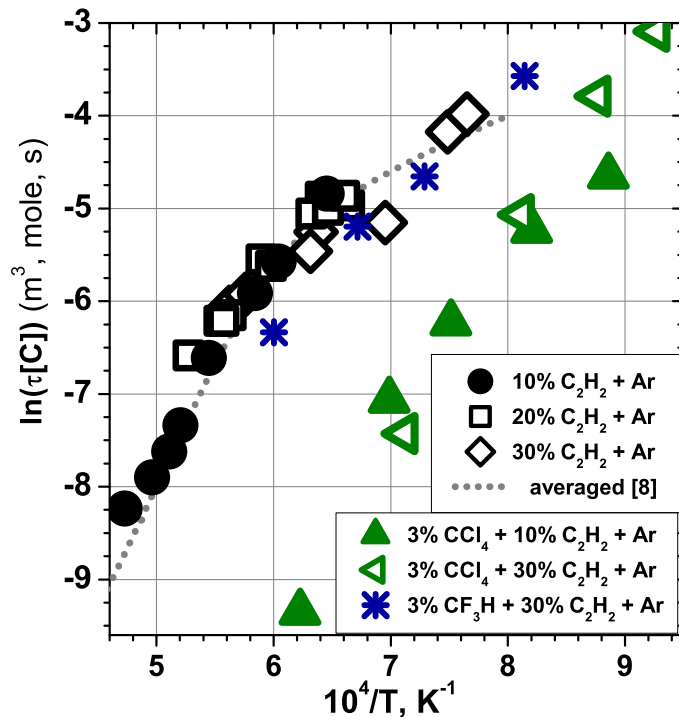


Figure 5. Experimentally observed temperature dependencies (dots) of induction time of carbon particles formation.

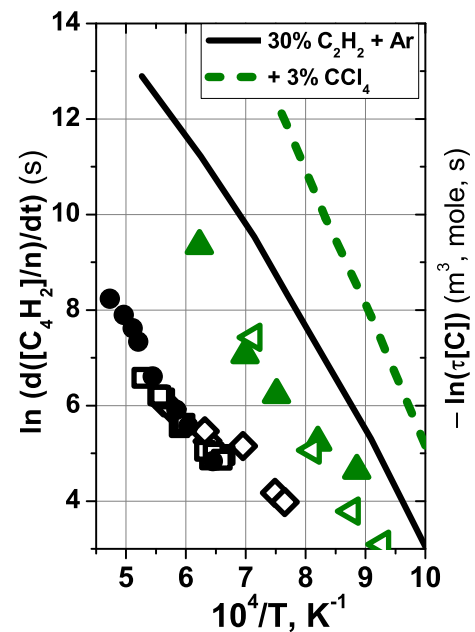
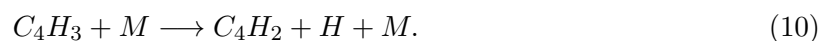


Figure 6. Modeled temperature dependencies (lines) of C_4H_2 formation rate and reversal induction times of carbon particle formation (dots; see figure 5 for designations).

because of the complexity of the reactions involved. An accurate calculation of temperature time profiles and a direct evaluation of induction times require quite complex consideration of large carbon clusters and even nanoparticles growth, as just at these stages of reaction the main heat release take place [7]. Therefore, for a rough analysis of the experimental results, the main kinetic processes determining the rates of active radical formation during acetylene pyrolysis were taken into account and kinetic modelling was limited by the simplest polyacetylene radical—diacetylene C_4H_2 formation. According to the results [15] at low temperatures ($T \leq 1800$ K) among the pyrolysis initiating reactions the next one is dominating:



which is immediately followed by rapid dissociation of $_{43}$:



Atomic hydrogen formed in reactions (9) and (10) is involved in a chain mechanism of acetylene decomposition:



The temperature dependence of characteristic rate of C_2H_2 decomposition is mainly determined by an activation energy of reaction (11), $E_a = 116$ kJ/mol [16], which is a bottleneck of the chain and in which the generation of biacetylene C_4H_2 proceeds. As it was shown in [17], C_4H_2 is the main species which determines subsequent particle formation; thus, one can assume that

the modelled dependences of C_4H_2 yield present a rough notion about particle formation in general.

As one can see from figure 5, the admixture of 3% CF_3H had no noticeable influence on the induction time of particle formation in the 30% C_2H_2 +Ar mixture. Such a result is in accordance with the absence of any reaction, which could provide some influence on the chain mechanism of acetylene decomposition in the web database [18]. Although the heat consumption of CF_3H decomposition could be significant, under the given conditions it is still negligible due to the high heat release of carbon condensation during pyrolysis of 30% C_2H_2 [7].

The promoting influence of CCl_4 evidenced by a significant decrease in the induction time of particle formation in the mixture containing 3% CCl_4 (see figure 4) could be explained by the reaction:



The C_2H radical formed in reaction (13) is subsequently involved in reaction (12) and initiates the chain decomposition of acetylene as described above (reactions (11)–(12)). Since the dissociation of hydrogen at the temperatures below 2000 K is negligible, such a reaction may have a dramatic influence on the atomic hydrogen concentration and, thus, the characteristic rate of acetylene decomposition and polymerization. One can see that the temperature dependences of induction times for acetylene mixtures with and without CCl_4 (figure 4) start to diverge at the temperatures around 1000 K, at which chlorine atom detachment from CCl_4 becomes fast enough to provide noticeable effects in a shock tube experiment [19]. According to [18], atomic chlorine is the only pyrolysis product which can react with acetylene.

CCl_4 decomposition has been described by a detailed multi-stage kinetic model. Since there are currently no thoroughly tested conventional models of CCl_4 pyrolysis, the reactions were collected from several sources including [19–22]. The thermodynamic properties of the included species were taken from [20, 23]. The suggested resulting mechanism was validated using CCl_4 , Cl_2 and C_2Cl_2 time profiles from recent work [24]. The main pathway of CCl_4 decomposition under the given conditions is:

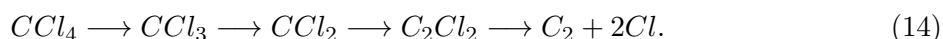


Figure 6 represents the modeled temperature dependence of the rate of C_4H_2 formation $d[C_4H_2]/(n \cdot dt)$ (n —total concentration of the mixture) for the mixtures 30% C_2H_2 +Ar and 3% CCl_4 +30% C_2H_2 +Ar. A good correlation between the temperature dependencies of the experimental reversal induction times of particle formation and the modeled rates of C_4H_2 formation (figure 6) was observed, especially in the high temperature region and, thus, relatively short induction times (1–100 μs). The influence of the chlorine-containing admixture—i.e., a steeper temperature dependence of the induction time, shifted to lower temperatures—is very well described by the model.

3.3. Superrich acetylene mixtures

As it was shown that CCl_4 has counter influence on oxygen-free and stoichiometric acetylene mixtures, analysis of its action on ignition and particle formation in superrich acetylene–oxygen mixtures can add to the general understanding of the mechanism of its influence on the development of acetylene combustion and polymerization reactions and carbon particle formation. The values of induction time of carbon particle formation obtained in pilot experiments in superrich acetylene–oxygen mixtures, particularly doped with CCl_4 , are presented in figure 7. One can see that the admixture of 1–3% O_2 causes noticeable shift of temperature dependence to the lower temperature region. Its value is linearly proportional to oxygen concentration and it is in a good agreement with the estimations of heat release in acetylene oxidation. Thus, one can assume that oxygen presence can be considered just as

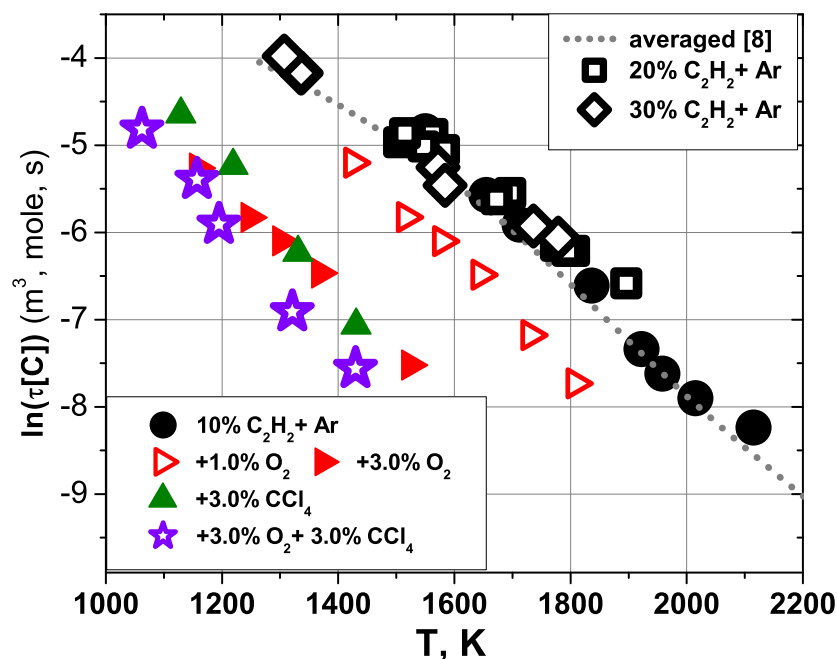


Figure 7. Experimentally observed temperature dependences of induction time of carbon particles formation in superrich acetylene–oxygen mixtures.

a cause of a rapid change of the mixture temperature and barely affects following acetylene polymerization kinetics. Addition of 3%O₂ to the mixture 3%CCl₄+10%C₂H₂+Ar, though, changes the induction time values just slightly. Obvious explanation is the suppression influence of CCl₄ (see figure 4) which actually leads to comparable characteristic times of acetylene oxidation and carbon particle formation at given temperatures.

4. Conclusion

The influence of CF₃H and CCl₄ admixtures on acetylene ignition and pyrolysis behind shock waves was experimentally investigated. Minor inhibiting effect of CF₃H on ignition stoichiometric acetylene–oxygen mixtures was observed; presence of CCl₄ increases ignition delay times significantly. Adding of 3% CF₃H had no noticeable influence on the induction time of carbon particle formation in the 10–30%C₂H₂+Ar mixtures, while 3% CCl₄ admixture had dramatic promoting effect and reduced induction time by approximately one order of magnitude. The promoting influence of CCl₄ on carbon condensation during acetylene pyrolysis could be explained by the reaction $C_2H_2 + Cl \rightarrow C_2H + HCl$ and following involvement of C₂H in chain mechanism of acetylene decomposition. Results of kinetic modeling performed using the suggested mechanism, agree well with experimental results.

Acknowledgments

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