

Soot Formation in the Pyrolysis of Halogenated Hydrocarbons. Part I, Binary Mixtures of Carbon Tetrachloride with Hydrogen and Iron Pentacarbonyl

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Measurements on carbon particle growth during CCl_4 thermal decomposition were carried out behind both incident and reflected shock waves. Three kind of mixture compositions have been investigated: 4000 ppm CCl_4 in argon; 200 to 4000 ppm CCl_4 and 200 to 8000 ppm $\text{Fe}(\text{CO})_5$ in argon; 4000 ppm CCl_4 and 4000 ppm hydrogen in argon. The temperature range $1200 < T/\text{K} < 3200$, pressure around 25 bar. Kinetics of the particle growth was detected via the attenuation of the laser beam (He-Ne laser, 632.8 nm).

The low temperature boundary for soot particles detection and magnitude of soot yield in CCl_4 pyrolysis is the same as that for most of the hydrocarbons studied. The temperature change during CCl_4 pyrolysis is an important factor for its kinetic interpretation. The first order rate constants of soot growth $k_f/[\text{C}]$ are higher than those for all hydrocarbons, including benzene under comparable conditions. At $T < 2200$ K the induction times t_{ind} are close to those for hydrocarbons with respect to both, absolute values and activation energy. In the middle temperature range studied, $2200 < T/\text{K} < 2500$, an "induction-less behaviour" of soot growth was observed; t_{ind} at $T > 2500$ K show a negative activation energy. Hydrogen additives significantly act on soot formation characteristics depending on H/Cl-ratio.

Chemical reaction in mixtures $\text{CCl}_4/\text{Fe}(\text{CO})_5$ was observed even at relatively low temperatures behind incident shock waves. However, iron additives only slightly change the soot yield as compared to CCl_4 pyrolysis.

A qualitative interpretation of experimental findings observed is suggested based on the consideration of the hierarchy of characteristic times in reacting systems followed by the growth of soot particles.

Introduction

Chlorinated hydrocarbons are among the main constituents of many industrial wastes and they may influence soot formation in industrial incinerators [1]. Peculiarities of soot formation from chlorinated hydrocarbons are also of interest from a fundamental point of view.

Study of the soot formation in binary mixtures often can give additional insight into the interplay of different factors in the course of soot growth. It was shown that iron-bearing compounds are most effective metal additives. In particular, the significant promotion action of $\text{Fe}(\text{CO})_5$ on soot formation in C_2H_4 pyrolysis was revealed and explained as influence of iron clusters which may provide the active sites for soot growth [2]. Hydrogen additives significantly suppress the soot yield in C_2H_2 pyrolysis [3]. The influence of H_2 and $\text{Fe}(\text{CO})_5$ on soot formation for chlorinated substances was not yet studied.

It is well known that soot formation during hydrocarbon combustion and pyrolysis behind shock waves can be

characterised by several features. Firstly, this process is limited by temperature boundaries which were determined extensively in shock waves and also in flames [4]. However, the data on these boundaries in some cases differ significantly, in particular depending on specificity of experimental techniques used to detect soot yield. As a consequence, there is no generally accepted point of view on the physical meaning of these boundaries. Nevertheless, the appearance temperature of soot, T_{ap} , is among the interesting characteristics especially from a practical point of view. Secondly, time evolution of soot growth during hydrocarbon pyrolysis behind shock waves shows some general features: Induction period, selfacceleration stage and growth to steady state level.

Soot formation in the pyrolysis of chlorinated methane, their mixtures with methane, and chlorinated ethylene was studied in [5]. The amount of soot produced in the pyrolysis of chlorinated hydrocarbons is larger than that formed in normal hydrocarbons. The soot yield in CCl_4 pyrolysis observed in [5] was however small and shifted to rather high temperatures $T > 2500$ K. That was different from the typical behaviour of other chlorinated methane's. However, these above mentioned data were obtained in mixtures with a high percentage of CCl_4 in the mixture (9.6%) and nonisothermicity during pyrolysis could be

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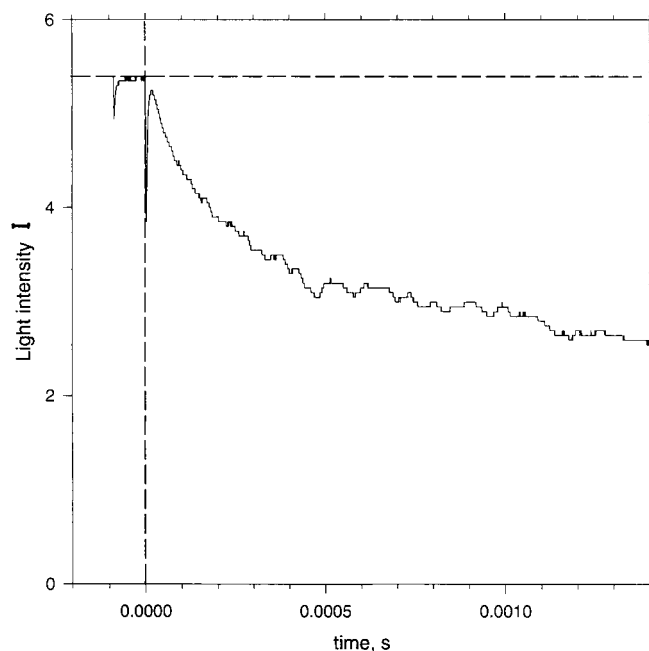


Fig. 1
Absorption record during CCl_4 pyrolysis behind reflected shock wave. 4000 ppm CCl_4 in argon, $T=2260$ K, $P=23.4$ bar

significant. Below we present some estimations confirming this point of view. On the other hand, one may expect that kinetically the CCl_4 pyrolysis is a rather simple system, at least for the early stages of the reaction [6], and should give a good chance to find main kinetic contributions leading to carbon particle growth.

Apparently, to avoid large temperature changes in the course of pyrolysis followed by subsequent soot formation and related with this uncertainties in the interpretation of primary experimental data it is necessary to perform experiments at high pressure with low percentage of sooting molecules in the mixture. In line with these arguments the principal objective of this work is two-fold. Firstly, to measure the temperature boundaries and kinetic parameters for carbon particle growth during CCl_4 decomposition with and without additives of H_2 and $\text{Fe}(\text{CO})_5$. Secondly, to compare these experimental findings with the existing data for soot growth during the pyrolysis of hydrocarbons and their halogenated counterparts in order to estimate the common kinetic driving forces leading to carbon growth.

Experimental

The experimental installation has been described elsewhere [7], and only some details are given here. The main part of measurements were performed behind reflected shock waves in 70 mm i.d. steel shock tube with a 4.5 m long driver section and 28 mm thick tube wall. The shock wave velocity was measured by Kistler pressure gauges and shock wave gas parameters were calculated in the ordinary manner [7]. The mixtures being investigated were prepared manometrically and mixed by convection in stainless steel cylinders at least 48 h before

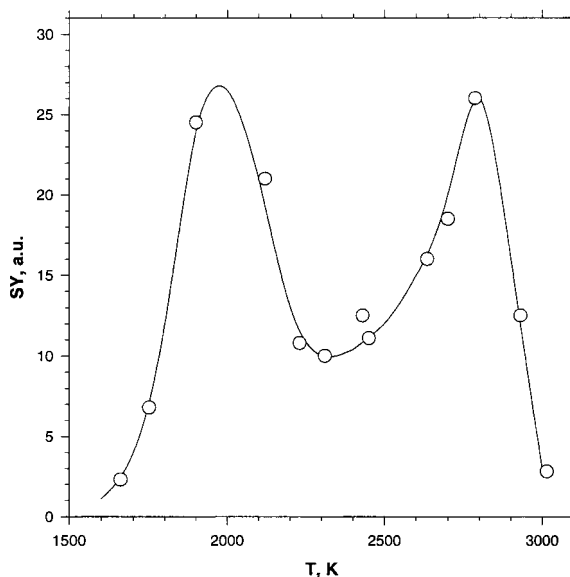


Fig. 2
Soot yield SY in arbitrary units during CCl_4 pyrolysis; measurements behind a reflected shock wave at 1 ms

use. Diluent gas argon (>99.998% Messer-Griesheim) was used without further purification. Carbon tetrachloride and iron pentacarbonyl (Fluka) were distilled in a liquid nitrogen trap. The samples were frozen and then the middle fraction was evaporated in the mixture cylinder. Measurements on carbon particle growth during CCl_4 thermal decomposition were carried out behind both incident and reflected shock waves. Three kind of mixture compositions have been investigated:

- 4000 ppm carbon tetrachloride in argon;
- 200 to 4000 ppm carbon tetrachloride and 200 to 8000 ppm iron pentacarbonyl in argon;
- 4000 ppm carbon tetrachloride and 4000 ppm hydrogen in argon.

The temperature range was $1200 < T/\text{K} < 3200$, pressure around 25 bar. Kinetics of the particle growth was detected via the attenuation of the laser beam (HeNe-Laser, 632.8 nm). The light extinction traces were converted into soot profiles using Beer's law (see e. g. [7]).

Experimental Results

Carbon Tetrachloride

Absorption traces observed during CCl_4 pyrolysis are similar to that for hydrocarbon pyrolysis with some peculiarities which are described below. Absorption traces of soot formation during hydrocarbon pyrolysis (see e. g. [7]) give in fact three parameters characterising soot formation: Induction time t_{ind} , soot growth rate k_f and soot yield SY.

In the middle temperature range studied, $2200 < T/\text{K} < 2550$, the soot particle growth starts just behind the reflected shock front without prominent induction period (Fig. 1) and the absorption curve may be well approxi-

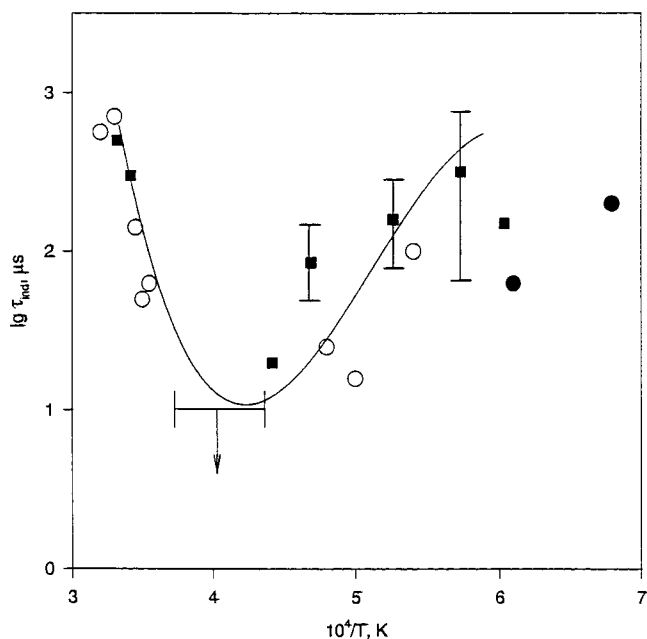


Fig. 3
Temperature dependence of induction times of soot formation in different mixtures in argon ○ 4000 ppm CCl_4 and 400 ppm $\text{Fe}(\text{CO})_5$, ● 4000 ppm CCl_4 and 4000 ppm H_2 , ■ 4000 ppm CCl_4

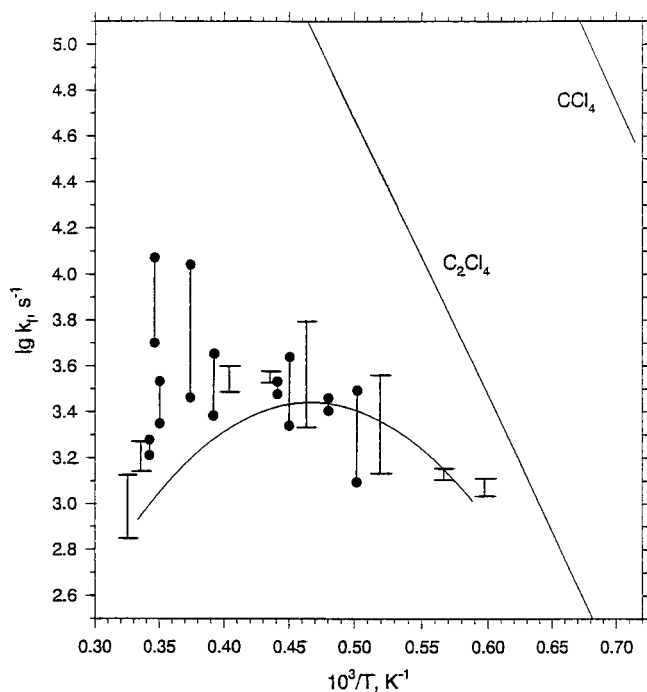


Fig. 4
Temperature dependence of the soot formation constant k_f . Points: experimental data, upper and lower points correspond to bi-exponential soot growth, □ 4000 ppm CCl_4 , ● 4000 ppm CCl_4 and 400 ppm $\text{Fe}(\text{CO})_5$ in argon. Lines: decomposition rate constants for C_2Cl_4 and CCl_4 accounted for fall-off behaviour

mated by the usual growth profile of the soot volume fraction $f_v(t) \approx (1 - e^{-k_f t})$ where k_f is the first order rate constant of soot growth. The temperature dependencies of the above mentioned parameters are presented in Figs. 2

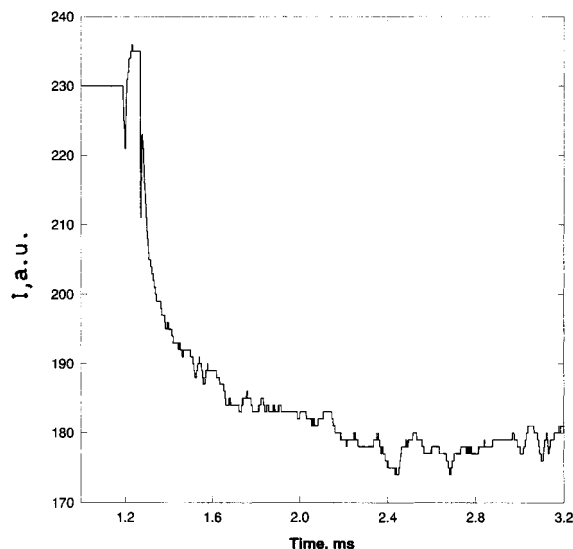


Fig. 5
Absorption record in mixture 4000 ppm CCl_4 and 4000 ppm H_2 behind reflected shock wave. $T=2230$ K, $P=25.5$ bar

to 4. It is well known that the temperature dependence of SY values for hydrocarbon pyrolysis shows single bell shaped curves (see e.g. [7]). However, for the mixture 4000 ppm CCl_4 in argon the picture is more complicated (Fig. 2) and we can describe the observed soot yields as a superposition of two soot bells with a local minimum at T around 2300 K. The temperature boundary for soot appearance is around 1600 K. Note that the position of this minimum for SY is the same as that for the maximum of k_f , however for SY the minimum is more prominent. Additional experiments in this temperature range are needed to obtain more reliable data on the temperature dependent k_f . In experiments at $T < 2200$ K and $T > 2550$ K the induction periods (Fig. 3) t_{ind} may be determined in the ordinary manner (see e.g. [7]), however they could not be determined as clearly as in hydrocarbon pyrolysis.

Influence of Hydrogen

Absorption traces in mixtures containing 4000 ppm CCl_4 and 4000 ppm H_2 (Fig. 5) exhibits the same properties as for CCl_4/Ar with more noticeable soot propensity because soot growth was detected already at lower temperatures. As can be seen from Figs. 3 and 6, hydrogen additives affect soot formation parameters drastically:

- Large shifting of the soot bell to lower temperatures. T_{ap} is around 1200 K and the maximum of increased SY is at 1600 K.
- The second soot bell disappears completely.
- Induction times are shorter as compared to mixture 4000 ppm CCl_4 in argon (Fig. 3).

Moreover, the colour of the deposit on the walls and the end plate of the shock tube after an experiment was softly lemon yellow or sometimes with golden iridescent. The colour of the carbon deposit is dependent on the H/Cl-

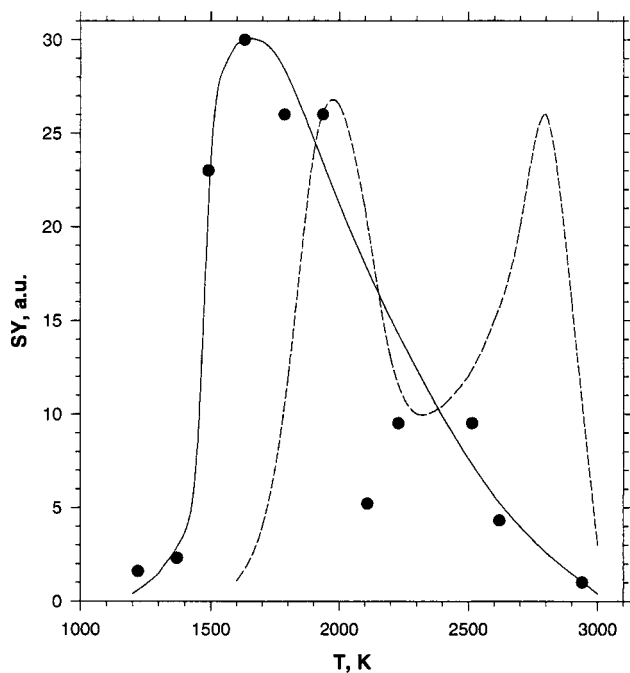


Fig. 6 Soot yield SY in arbitrary units for mixture 4000 ppm CCl_4 and 4000 ppm H_2 (points) corresponding to 1 ms reaction time behind the reflected shock wave. Dotted curve: approximation of experimental data for mixture of CCl_4/Ar

ratio. Further studies of dependencies of colour and other soot formation parameters at a broad variation of the H/Cl-ratio should be certainly interesting. Contrary, complete soot suppression was observed for larger additions of H_2 . With 10% H_2 we did not observe any soot formation.

Mixtures of Carbon Tetrachloride with Iron Pentacarbonyl

Absorption traces in $\text{CCl}_4/\text{Fe}(\text{CO})_5$ mixtures show an initial signal related with the iron cluster contribution (Fig. 7), because the $\text{Fe}(\text{CO})_5$ thermal decomposition followed by iron vapor nucleation is very fast under the conditions applied [2]. However, when the ratio of Fe/Cl becomes smaller the initial absorption behind the incident shock wave is very small compared with the reference experiments without CCl_4 . This observation certainly shows that the nascent iron-atoms efficiently react with CCl_4 molecules forming probably some kind of iron chlorides and these reactions compete with the iron nucleation.

The result of the reaction between iron-bearing species and CCl_4 is clearly seen from a comparison of the absorption behind incident shock waves in different mixtures (Fig. 8). The mixture of 4000 ppm $\text{Fe}(\text{CO})_5$ in argon demonstrates the high reproducibility of the absorption records at 25 bar and gives a reference level of the steady state optical absorbance reached after $\text{Fe}(\text{CO})_5$ decomposition of $D_2=0.60\pm 0.2$. Additives of CCl_4 diminish the absorption, depending on the CCl_4 content and the tem-

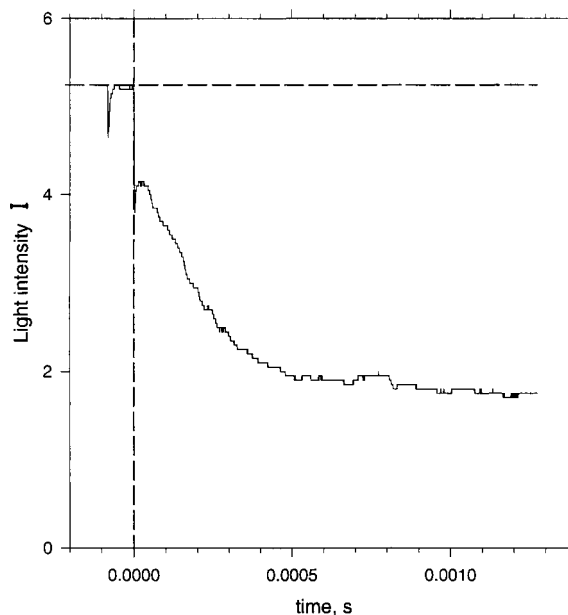


Fig. 7 Absorption record in mixture of 4000 ppm CCl_4 and 400 ppm $\text{Fe}(\text{CO})_5$ behind reflected shock wave. $T=2690$ K, $P=22.9$ bar

perature. The decay of the absorption is about proportional to the CCl_4 content and is increasing with the rise of temperature. Asymptotically, the resulting decrease of the absorption nearly ceases at $T < 1250$ K if the Fe/Cl-ratio is around $0.2 < \text{Fe}/\text{Cl} < 0.5$.

Now the time behaviour of the absorption in $\text{CCl}_4/\text{Fe}(\text{CO})_5$ mixtures shall be considered. At low and high temperatures studied clearly two parts of absorption records were observed (Fig. 9) so that the soot volume fraction $f_v(t)$ growth may be approximated as the sum of two terms.

$$f_v(t) = A_1(1 - e^{-k_{f1}t}) + A_2(1 - e^{-k_{f2}t}), \quad (1)$$

where k_{f1} and k_{f2} are the soot growth rates for first and second stages, respectively. Therefore, the processing of such absorption traces in accordance with the procedure described [7] leads to two values of the “first-order soot rates”. At middle temperatures, $2200 < T/\text{K} < 2300$, the two exponents nearly merge in a single exponential profile and the absorption records look like the yield of a simple quasi first order reaction. This feature is evidently different from the typical traces during hydrocarbon pyrolysis which exhibit clearly expressed induction kinetics followed by a S-shaped selfacceleration stage and then the final part with single first order rate for soot growth. Temporary characteristics of absorption traces depend on temperature and Fe/Cl-ratio. Single exponential behaviour is mostly evident in the middle temperature range $2200 < T/\text{K} < 2500$. The biexponential behaviour was observed at high temperatures $2500 < T/\text{K} < 3000$ and less evident at low temperatures $T < 2200$ K.

Fig. 9 illustrates the determination of soot growth rates f_{f1} and f_{f2} as slopes of the appropriate parts of the whole

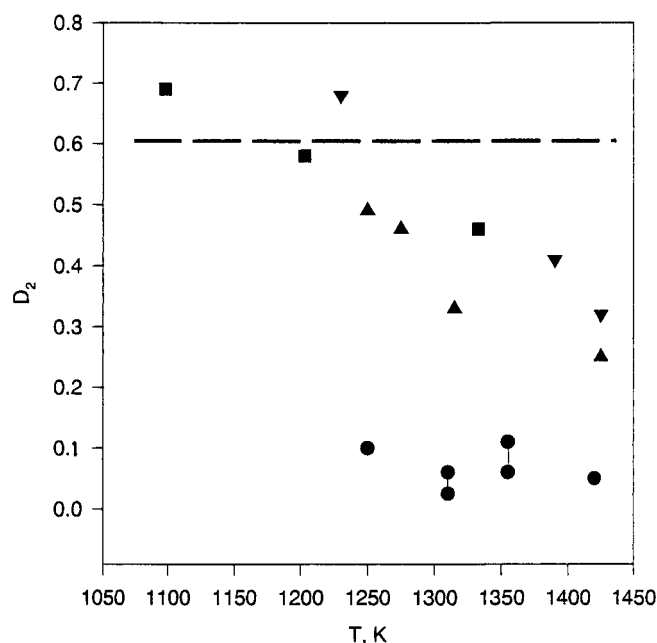


Fig. 8
Steady state level of the absorbance D_2 behind incident shock waves in different mixtures of CCl_4 with 4000 ppm $\text{Fe}(\text{CO})_5$ in argon. Dotted line corresponds to iron clusters absorption without CCl_4 . ● 4000 ppm, ■ 1600 ppm, ▲ 800 ppm and ▼ 400 ppm CCl_4

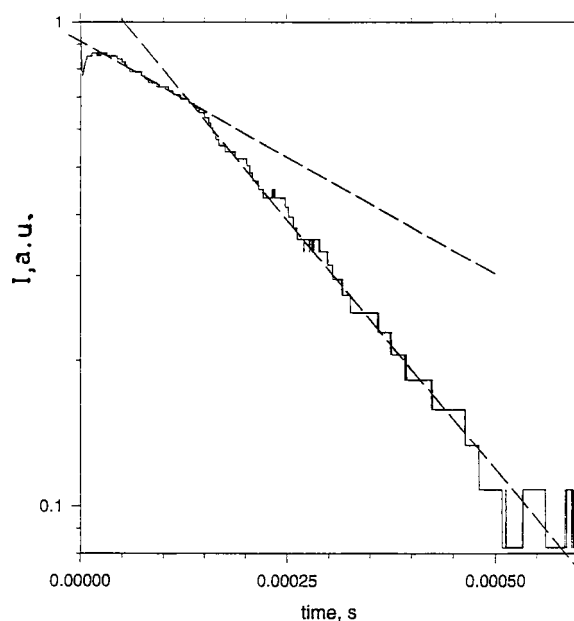


Fig. 9
Semilogarithmic plot of the absorption record (Fig. 7) illustrating bi-exponential behavior of soot growth. Mixture: 4000 ppm CCl_4 and 400 ppm $\text{Fe}(\text{CO})_5$, $T_5=2686$ K, $P_5=22.9$ bar. (See text about determination of time duration of induction period)

curve (see Fig. 4). If the induction period t_{ind} is determined as the duration between zero time and the interception of straight lines with initial absorption level we can see in fact some uncertainties in this case. For the first stage τ_{ind} is short and close to the time resolution, taking into account schlieren spike and noise level. For the second stage τ_{ind} is more prominent but it may be considered as a consequence of the two stage behaviour of soot growth. Therefore, when the difference between the time characteristics of the two stage behaviour is quite large (e.g. first part of exponential growth is rather slow) the absorption traces may be easily used for conventional treatment to find incubation times in the ordinary manner. The appropriate results are presented in Fig. 3. At middle temperatures the range of inductionless behaviour is shown by a horizontal bar. The negative temperature dependence of the induction time at $T > 2500$ K is completely unusual for soot formation in hydrocarbons.

Note that at temperatures around $2500 < T/\text{K} < 2800$ the $\text{Fe}(\text{CO})_5$ additives (400 ppm) produce certainly higher k_f values as compared to mixtures of 4000 ppm CCl_4 in argon (Fig. 4). Accordingly, the soot yield SY observed in the same mixtures shows a slight increase at the same temperature region (Fig. 10). As can be seen also, in the temperature range of the first soot bell the influence of 400 ppm $\text{Fe}(\text{CO})_5$ is small. That is in contrast to the $\text{Fe}(\text{CO})_5$ promotion action on soot growth during ethylene decomposition [2]. In mixtures with relatively high content of $\text{Fe}(\text{CO})_5$ the experimental points of SY are shifted to higher temperatures as compared to the reference mixture 4000 ppm CCl_4 in argon.

Discussion

The first systematic study of soot formation during shock tube pyrolysis of chlorinated hydrocarbons was undertaken in [5]. The high sooting propensity of chlorinated hydrocarbons has been attributed to a weaker C–Cl bond compared to a C–H bond. The weaker C–Cl bond leads to a relatively high Cl-atom concentration in sooting reaction system. Some tentative mechanism was suggested to explain an observations in [5] of higher sooting tendency of methyl chloride compared to methane due to chlorine catalysed formation of C_2H_3 and C_2H_2 . To explain the higher sooting tendency of dichloromethane compared to that of methylchloride, the higher concentrations of Cl-atoms and as a consequence the higher rate of chlorine catalysed production of C_2H_2 , C_2H and C_2H_3 in the former case was assumed [5]. Further, the important role of CHCl radical leading to C_3H_3 through reaction



was suggested. Rapid formation of C_3H_3 initiates an efficient pathway to soot, because the propargyl radical recombination is considered to be a dominant way to first aromatic ring formation. These arguments may explain the outstanding sooting propensity of dichloromethane. Since the authors of [5] observed the soot yield in CCl_4 pyrolysis shifted to temperatures higher than 2400 K, they assumed the existence of another mechanism for soot formation at high temperatures. This mechanism was assumed to proceed through C_2 addition, whose formation is thermodynamically favourable at high temperatures.

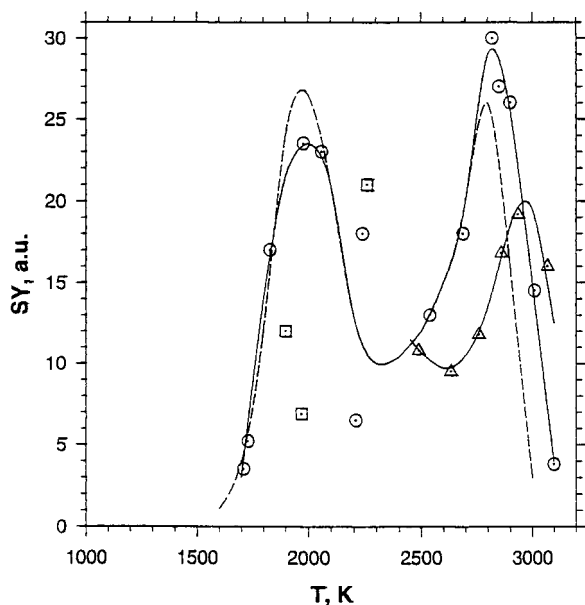


Fig. 10
Temperature dependence of soot yield in different mixtures of 4000 ppm CCl_4 with $\text{Fe}(\text{CO})_5$. Reaction time behind reflected shock waves corresponds to 1 ms. Dotted line corresponds to soot yield without $\text{Fe}(\text{CO})_5$. \circ 400 ppm, \square 3000 ppm and \triangle 4000 ppm $\text{Fe}(\text{CO})_5$

Concerning the SY in CCl_4 pyrolysis we have to state the difference of our results with data of [5]. Firstly, we measured “two-bell” soot yield profile as a function of temperature behind reflected shock waves (Fig. 2). Secondly, the disposition of the first bell on the temperature axis and the magnitude of SY are in fact the same as that for most hydrocarbons being investigated. This is quite evident from the low temperature boundary of soot appearance under various conditions and for different sooting molecules. On the other hand, in [5] the soot yield in CCl_4 pyrolysis became measurable at $T > 2300$ K and is smaller than that for another chlorinated hydrocarbons by about one order of magnitude.

Our explanation of that difference is related mostly with nonisothermal effects under the experimental conditions in [5]. Indeed, a high percentage of CCl_4 (9.3%) in mixture with argon may lead to significant cooling of the gas behind the shock wave due to fast decomposition of CCl_4 and even its fragments. As a result of this effect the soot formation in the above mixtures occurred at temperatures significantly lower than those calculated from a shock velocity measured assuming no reaction behind the shock wave. To estimate the magnitude of cooling we need to take into account the heat of the decomposition reactions and the characteristic reaction times. The comparison between CCl_4 and C_2Cl_4 decomposition rate constants and soot growth rates (Fig. 4) shows clearly that the former processes are much faster.

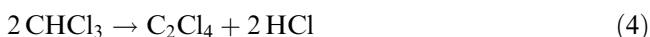
According to our estimations the temperature decay in experiments [5] with mixture 9.3% CCl_4 in argon may be about 500 K if the first stage of relatively fast reactions

goes into the transient products according to the following overall scheme



The reaction enthalpie is ($\Delta H = 146$ kJ/mol). If we assume that the ratio of concentrations $\text{Cl}/\text{Cl}_2 \approx 0.25$ the estimated temperature drops even more, around 600 K. If we take into consideration these corrections the data [5] agree well with our measurements of T_{ap} . Anyway, the correct simulation of experimental data [5] concerning SY in CCl_4 pyrolysis was to consider nonisothermal situation behind the shock wave.

Note in this connection that experiments with partly chlorinated hydrocarbons for which heat losses in dissociation of parent molecules were compensated by heat release in exothermic steps with HCl production give more realistic value for soot appearance temperatures (see [5]) despite of the fact that the measurements were performed in mixtures with high percentage of reactants. In particular, similar estimations for decomposition of CHCl_3 according to the overall scheme



give in fact a thermoneutral ($\Delta H = 10$ kJ/mol) result.

Turning to measurements of the appearance temperature for soot formation behind shock waves, it is necessary to note that the experiments at high pressure with highly diluted mixtures are a reliable approach to obtain the correct values for T_{ap} . Comparison of existing data in flames and shock waves shows that T_{ap} is around 1600 K for all hydrocarbons and chlorinated hydrocarbons being investigated and probably may be considered as a relevant overall parameter corresponding to the critical condition for beginning of soot inception in shock waves experiments. Finally, we need to emphasise the necessity to take care when we use such parameter as T_{ap} . Apparently, this value is in relevant connection with the residence time t_{res} of gas particles in the reaction zone. Once the characteristic scale of t_{res} is approximately equal 1 ms for experiments in shock waves and has the same order of magnitude for flame experiments [4], this circumstance may explain the reasonable consistency of T_{ap} data for both methods. In experiments with higher t_{res} , e.g. flow or static reactors, lower values of T_{ap} may be found.

Turning again to the two-bell SY curve and the temperature dependence of k_f we need to compare also the ratio of chemical rates for some species which may be considered as rate controlling for soot formation. The representative picture of the hierarchy of several dominant kinetic processes may be seen from Fig. 4 which shows that at the beginning of soot formation even at the low temperature boundary (1600 K) the parent CCl_4 molecules are “completely” converted to C_2Cl_4 and its thermal decomposition plausibly gives a limiting step for the soot embryo production at least at lower temperature near T_{ap} . Considering the two-bell shape of SY curve observed in

CCl_4 pyrolysis, we assume that the second bell is related to the reaction behind the incident shock wave¹ when the mixture composition entering in front of the reflected shock wave significantly differs from the initial CCl_4 mixture being enriched (or may be replaced) by such components as C_2Cl_4 and C_2Cl_2 molecules, radicals as C_2Cl_3 and C_2Cl , and Cl-atoms.

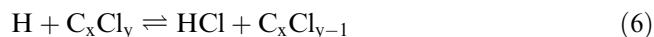
Characteristic times for CCl_4 pyrolysis are 2 to 3 orders of magnitude shorter than those for most of the sooting pyrolytic systems under comparable conditions. Therefore, it allows to consider the overall reaction proceeding in two stages. The first one (relatively fast period) with the establishment of partial equilibrium within the radical pool and molecules with double and triple C–C-bonds, i. e., C_2Cl_4 , C_2Cl_2 . The second one (slower) is in fact rate limiting for carbon particle growth when the soot building material is produced in reactions between the above mentioned radicals and molecules.

As can be seen from Fig. 4 the normalized $k_f/[C]$ values for soot ($[C]$ is the total carbon concentration) formation during carbon tetrachloride pyrolysis is rather high, around $5 \cdot 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at $T=2000 \text{ K}$. It is interesting to compare the absolute magnitudes of k_f with that for another molecules under comparable conditions behind shock waves. A comprehensive set of appropriate data is presented in [8, 9]. The maximum values of $k_f/[C]$ are as follows: $5 \cdot 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for C_7H_8 , $2 \cdot 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for C_8H_8 , $6 \cdot 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for C_2H_2 and $4 \cdot 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for C_2H_4 at temperature around 1900 K . Thus, $k_f/[C]$ for soot formation during carbon tetrachloride pyrolysis is among the highest as compared with other molecules being studied under comparable conditions. Note that similar large values of $k_f/[C]$ were observed in soot formation during ethylene pyrolysis catalysed by $\text{Fe}(\text{CO})_5$ additives [2].

The temperature dependence of the first order soot rate shows the typical bell shaped curve for the base mixture of 4000 ppm CCl_4 in argon, though at high temperature $\text{Fe}(\text{CO})_5$ additives exhibit certainly higher $k_f/[C]$ values. Action of hydrogen additives is apparently related with the effective formation of H-atoms and further reactions. Indeed, the reaction

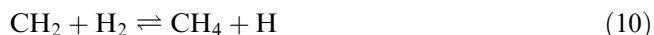


gives fast generation of H-atoms which in turn react via



Otherwise, the small additive concentrations of H_2 act as promoting factor through the binding of two Cl-atoms and increasing of C/Cl-ratio to more favourable magnitude. The above mentioned formation of CHCl radicals may also be responsible for a promotion effect provided

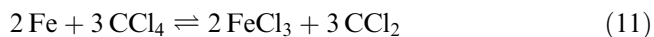
that the ratio of H_2 and CCl_4 is optimal. For large hydrogen concentrations, $[\text{H}] \gg [\text{Cl}]$, the observable soot suppressing effect may be explained as follows. If H_2 is in excess the formation of soot precursors cannot compete with faster reactions leading e. g. to formation of CH_4 , via the reactions:



As a result a significant part of carbon converts to CH_3 and CH_4 during the residence time for the experiments behind shock waves (around 1 ms). In other words, at given temperatures there is not enough reaction time for soot growth. These qualitative arguments will be verified by further numerical modeling.

The first indication on induction-less soot formation in C_2H_4 pyrolysis with $\text{Fe}(\text{CO})_5$ additives was shown in [2] and was treated as carbon particle growth on the iron cluster surface. Here, in addition to a similar phenomenon in binary mixtures $\text{CCl}_4/\text{Fe}(\text{CO})_5$, presumably also connected with microheterogeneous iron cluster contribution, we observed induction-less biexponential carbon formation in CCl_4 pyrolysis, that is not connected with iron clusters and must be explained by another reason. Experimental findings and qualitative considerations on soot formation during CCl_4 pyrolysis and its mixtures with $\text{Fe}(\text{CO})_5$ and H_2 are the background for computer modelling which are under way.

Let us discuss shortly the findings related with $\text{Fe}(\text{CO})_5$ additives. As was demonstrated earlier, the absorption records in binary mixtures $\text{CCl}_4/\text{Fe}(\text{CO})_5$ manifest chemical interaction between these components. Presumably, this effect is related with reactions of iron-atoms which appear due to fast $\text{Fe}(\text{CO})_5$ decomposition. The rate constant of $\text{Fe}(\text{CO})_5$ thermal decomposition is much higher than that for CCl_4 . Nascent iron-atoms may easily react with CCl_4 in accordance with the scheme in Table 1. For the thermochemical data see e. g. [10]. Reactions included in this scheme are exothermic or slightly endothermic. That permits to suggest reasonably fast occurrence of these reactions at $T > 1600 \text{ K}$. The averaged heat effect for the overall reaction



is equal to -555 kJ/mol . However, boiling points for FeCl_2 and FeCl_3 are rather different and equal to 1300 K and around 590 K , respectively [11]. Therefore, it is reasonable to expect that nascent FeCl_2 molecules may nucleate at $T < 1300 \text{ K}$. Observable characteristics of absorption behind incident shock waves agree well with this suggestion.

¹ This is confirmed by recent measurements of Tanke and Tsuboi, which show that for soot formation from CCl_4 after incident shock waves the second ‘‘SY bell’’ is not observed

Table 1
Reaction scheme of iron-atoms with CCl₄

Reaction	$\Delta_r H_{298}$ [kJ/mol]
Fe + CCl ₄ ⇌ FeCl + CCl ₃	+13
Fe + CCl ₃ ⇌ FeCl + CCl ₂	-80
FeCl + CCl ₄ ⇌ FeCl ₂ + CCl ₃	-217
FeCl + CCl ₃ ⇌ FeCl ₂ + CCl ₂	-310
FeCl ₂ + CCl ₄ ⇌ FeCl ₃ + CCl ₃	+66
FeCl ₂ + CCl ₃ ⇌ FeCl ₃ + CCl ₂	-27

Concluding Remarks

The most distinct peculiarities of soot formation in CCl₄ pyrolysis and mixtures of CCl₄ with H₂ and Fe(CO)₅ are as follows:

- The lower temperature boundary for soot particles detection and the magnitude of soot yield in CCl₄ pyrolysis are the same as that for most of the hydrocarbons studied.
- A comparison of soot formation characteristics for highly and slightly diluted mixtures of CCl₄/Ar shows that the temperature changes during CCl₄ pyrolysis is an important factor for kinetic simulation.
- The first order rates of soot growth $k_f/[C]$ is higher than that for all hydrocarbons, including benzene under comparable conditions.
- At $T < 2200$ K the induction times are close to those for hydrocarbons with respect to both, absolute values and activation energy. In the middle temperature range studied, $2200 < T/K < 2500$ induction-less behaviour of soot growth was observed. t_{ind} at $T > 2500$ K shows a negative activation energy.
- Hydrogen additives significantly act on soot formation characteristics depending on the ratio of H and Cl.
- Chemical reaction in mixture CCl₄/Fe(CO)₅ was observed even at relatively low temperatures behind incident shock waves. However, iron additives only slightly change the soot yield as compared to CCl₄ pyrolysis.

A qualitative interpretation of features observed is based on the consideration of the hierarchy of characteristic times in the above given reacting systems followed by the growth of soot particles. To our point of view the consideration of this reacting system as a two-stage process is a promising way to explain quantitatively the biexponential time history of soot formation kinetics and the two-bell shaped curves for SY. First, a relatively fast stage consists of fission of C–Cl-bonds in parent molecules, self-reac-

tions between radicals and radical-molecule reactions. A significant part of the reaction flow goes to C₂Cl₄ formation. Concurrently soot embryo formation occurs followed by the sequential growth of soot particles via incorporation of C_xCl_y species into the carbon matrix. Radicals C₂Cl and C₂Cl₃ may be considered as the most plausible building blocks for soot growth during CCl₄ pyrolysis. Exhaust of building material of the above mentioned radical pool leads to a decreasing soot formation rate and SY in the first stage. The second stage is connected with significantly slower dissociation of intermediate C₂Cl₄ molecules and delayed formation of soot building material. This stage may be responsible for the second stage of the soot growth and second soot bell position on the temperature axis.

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