

ISOTHERMAL SOOT OXIDATION EXPERIMENTS WITH INTERMEDIATE GAS CHANGE IN A PERKIN-ELMER TGA6

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Two isothermal soot oxidation protocols were tested in a Perkin–Elmer TGA6: (1) the sample was heated under N₂ and then the reaction gas was introduced and (2) the sample was introduced after the empty furnace was heated under the reaction gas. The first protocol is common in soot oxidation studies, it gives a measure of the volatiles and is easier to handle, but as it is shown the determined reaction rate may be falsified by the O₂ concentration. Using gas analysis it was found that ~2000 s are necessary for the complete gas change in the instrument. An instrument specific correction function involving the O₂ concentration and reaction order n with respect to O₂ was developed which allowed the correlation of the rates measured with both protocols.

Keywords: evolved gas analysis, isothermal, oxidation, soot, TG

Introduction

The use of diesel vehicles is constantly increasing mainly due to their inherent advantages, which include fuel economy, durability, driveability, etc. [1]. The main issue concerning their use are the increased nitrogen oxides (NO_x) and particulate matter emissions (PM) [2]. Specifically, diesel PM represents an important health hazard a fact that has led the legislation to adopt stringent emission standards. Diesel particulate filters (DPF) are becoming wide spread as an effective measure to reduce PM emissions from diesel vehicles as they have filtration efficiencies close to 100% [3]. Due to the fuel penalty induced by the gradual loading of the filter, its periodical regeneration, i.e. the combustion of the accumulated particulates, is necessary [3]. It is therefore vital to fully understand, model and control the regeneration process in order to optimize the application and operation of DPFs both for lifetime durability and fuel economy purposes. Consequently, the study of soot combustion for the extraction of kinetic data that can be coupled in modelling tools is very important. Different experimental approaches have been used in the literature including thermogravimetric analysis (TG) [4–13], flow and bed reactors, etc. [14, 15].

When TG is used for the extraction of chemical kinetics data it has known experimental and computational difficulties that include control of the reactant atmosphere [16], rate-controlling mass and heat transfer limitations [7, 8] as well as the choice of the opti-

mal calculation method of the kinetic parameters, e.g. [17], which have led to extended debating about the reliability of its results. However, although TG cannot substitute in situ experiments, it is still an important experimental tool that has been used extensively for soot and carbon oxidation studies [e.g. 10, 13, 18], mainly because it represents a fast, economical and easy to use experimental solution.

Although it is common to run non-isothermal TG using the same reaction gas throughout soot oxidation [6, 13], also a number of isothermal studies of soot reactivity are found in literature [4, 5, 7]. Non-isothermal protocols are preferred because isothermal experiments necessitate more experimental time and more sample mass, while identical experimental conditions and homogeneous sample are also necessary. Also, in the case of exothermal reactions, such as soot oxidation, self-heating of the sample may occur leading to deviation from the desired isothermal conditions. However, the temperature gradients within the sample are often neglected. This can be justified for smaller initial sample masses [7] and/or slower reaction [19], e.g. at lower O₂ concentration. Then the decoupling of the effect of temperature and progress of reaction on the reaction rate and rate constant is possible. Finally and despite the above mentioned limitations, isothermal studies are considered generally better for determining kinetic rates [18] while they also facilitate the investigation and modelling of reaction gas diffusion in the solid sample.

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With respect to the procedural details of isothermal experiments it is important to minimise the portion of the sample mass that reacts during the furnace heat-up to the reaction temperature in order to have the same initial sample mass at every temperature and/or avoid total and fast reaction of very reactive samples. Experimentally, this can be achieved by either (1) heating up the sample in the presence of an inert gas and then introducing the reaction gas (Protocol 1 – Prot. 1) or (2) heating up the empty furnace in the presence of the reaction gas and then introducing the sample into the furnace (Protocol 2 – Prot. 2).

Both protocols have advantages and disadvantages, but since diesel soot may contain volatile material, some very reactive species and O_2 , it is common practice among researchers in this field to use Prot. 1 [4, 5, 7]. This combines a pre-treatment step which allows the adsorbed (usually reactive) species to be drawn away and oxidation of the sample in one run. Prot. 1 has also the advantage that the balance is allowed to stabilize before the beginning of the experiment and the sample remains in a controlled environment during the whole reaction. The opening of the furnace for sample introduction in the case of Prot. 2 may lead to uncertainties concerning the initial part of the reaction until the balance and the reaction chamber conditions stabilize. However, the accurate control of the reaction gas composition is the main issue for Prot. 1 since optimally the change of the sample atmosphere should take place instantaneously. In contrast in Prot. 2 the O_2 concentration remains the same throughout the measurement.

Consequently, TG's gas flow characteristics must be considered when kinetic experiments of this kind are conducted. Usually the balance and reaction gas flows are mixed [16] and the same gas must be used in both chambers in order to control the reactant concentration. In addition, when a gas change is to be made during the experiment the O_2 concentration restoration pattern must be explored. So, it is generally necessary to use gas analysis at the TG outlet.

In this context in the present study an experimental setup involving a conventional gas analyzer and dilution of the evolved gases is described and used for the study of the sample atmosphere in the Perkin-Elmer TGA6. Isothermal experiments with and without intermediate gas change were conducted and correlated at 3 different temperatures for 2 different soot samples. Because of the constant O_2 concentration present in the case of Prot. 2, the rates obtained thus are considered as a reference when comparing both protocols for the scope of the present study.

Methodology

Thermogravimetric analyzer (Perkin-Elmer TGA6)

In Perkin-Elmer TGA6 the balance and purge gas were controlled manually using a system of valves upstream of the instrument with the flow rate monitored through flow-meters separately for each chamber. In Fig. 1 [20] the instrument cross-sectional view shows the balance and sample compartments. A purge gas is forced through the balance chamber (flow rate $\sim 60 \text{ mL min}^{-1}$) for its protection. This stream flows into the sample chamber and is mixed with the reaction gas (flow rate $\sim 40 \text{ mL min}^{-1}$). Hence the gas that reacts with the sample is actually the sum of the two streams. Thus, for simplification it was decided to use the same gas through both chambers.

Evolved gas analysis

Figure 2 presents the gas analysis experimental setup used. CO_2 , CO and O_2 concentrations were measured online by a Horiba PG250 gas analyzer at the TG outlet. Since the analyzer pump requires 400 mL min^{-1} while the total TG flow rate is approximately 100 mL min^{-1} , it was necessary to dilute the evolved gases. Pure nitrogen (N_2) was used as a dilution agent

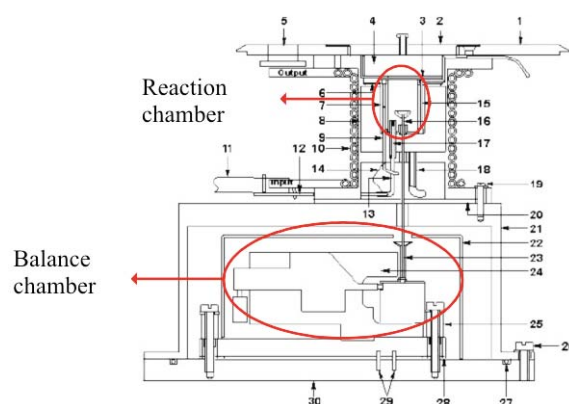


Fig. 1 Perkin-Elmer TGA6 cross-sectional view [20]

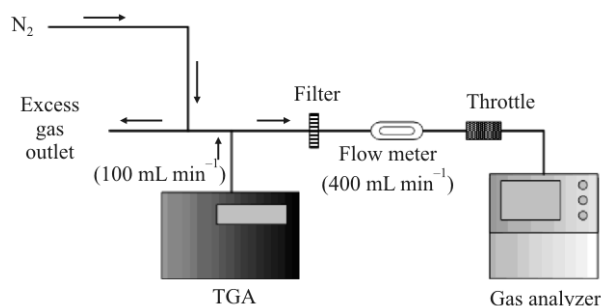


Fig. 2 Experimental setup

and excess N_2 flow was used to ensure that no ambient air was pumped into the dilution line. Synthetic gases of known O_2 concentration (nominal% O_2) have been used in the present study. Therefore, the dilution ratio (DR) could be defined by the raw (nominal% O_2) and diluted (measured% O_2) O_2 concentration measured after the completion of soot oxidation as follows:

$$DR = \frac{\text{nominal\% } O_2}{\text{measured\% } O_2} \quad (1)$$

Flow experiments

Dedicated tests were conducted at room temperature monitoring the O_2 concentration at the TG outlet after changing the gas flowing through the instrument. Bottles of synthetic gases (N_2 and 22% O_2/N_2) were connected to the valves placed upstream of the balance and the reaction chamber. Hence, the type of the gas flowing through each chamber could be controlled separately. For the tests N_2 was driven at first through both chambers. At a specific time point the gas that flowed either (1) only through the balance chamber, or (2) only through the reaction chamber or (3) through both chambers was changed from pure N_2 to 22% O_2/N_2 . Target of these tests was to examine if there is a specific pattern during the gas change and to define the time necessary for this change separately for the two flows.

Oxidation experiments

Isothermal soot oxidation experiments were conducted using the 2 protocols mentioned above:

(a) The sample was placed in the reaction chamber at ambient temperature and was heated under N_2 to the reaction temperature. Then the gas was changed from N_2 to the reaction gas (Prot. 1).

(b) The reaction chamber was heated empty up to the reaction temperature in the presence of the reaction gas. Then the sample was introduced into the reactor (Prot. 2).

A constant heating rate of $50^\circ\text{C min}^{-1}$ was used. 5 mg Printex U and 3 mg diesel soot samples were used. Printex U is commercial synthetic soot often used as a reference material in soot oxidation studies. Diesel soot was collected from a loaded DPF. No pre-treatment of the samples was done prior to the oxidation experiments. The experiments were conducted with the two protocols at 600–625–650°C/22% O_2 using both samples and at 650°C/4.5% O_2 only with Printex U.

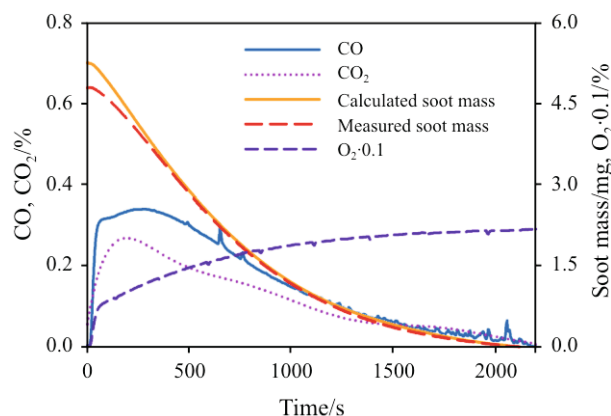


Fig. 3 Measured and calculated soot mass evolution for the oxidation of Printex U at 600°C/22% O_2 using Prot. 1

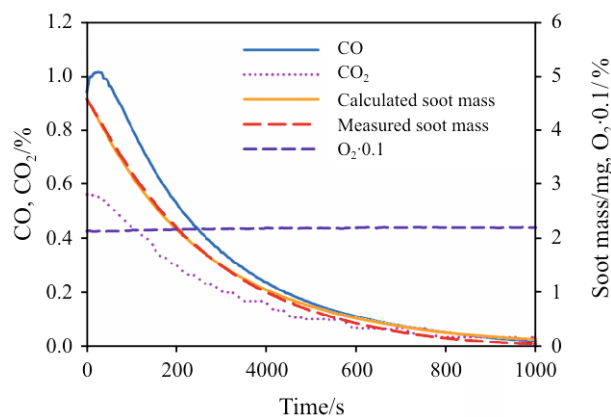


Fig. 4 Measured and calculated soot mass evolution for the oxidation of Printex U at 625°C/22% O_2 using Prot. 2

Results and discussion

Gas analysis setup reliability

The performance of the gas analysis setup was evaluated through comparison of the mass-time curve calculated via the CO/CO_2 balance and the measured curve of the TG. Figures 3 and 4 show the measured and calculated curves for 2 different characteristic cases of Printex U oxidation at 600°C with 22% O_2/N_2 using Prot. 1 and at 625°C with 22% O_2/N_2 using Prot. 2. For the measurement with Prot. 1 $t=0$ s is univocally defined by the change of the valve, while for the measurements with Prot. 2 $t=0$ s is defined after the balance reading and the dilution ratio are stabilized (typically about 60 s after the introduction of the sample). Thus, only the isothermal part of the measurements is presented. It is observed that the calculated soot mass reproduces fairly well the measured mass proving the overall reliability of the experimental setup.

O₂ concentration in the reaction compartment

As Fig. 3 shows, when using Prot. 1 the O₂ concentration at the outlet of the TG is not constant over time, i.e. the N₂ to reactant change does not occur instantly. In contrast, when using Prot. 2 it remains fairly constant with only a small concentration dip due to the soot combustion (Fig. 4).

Figure 5 presents the O₂ concentration measured after changing the gas from N₂ to 22% O₂/N₂ in two cases: (1) N₂ is flowing through the balance chamber and 22% O₂/N₂ is flowing through the reaction chamber and (2) vice versa. The composite curve resulting from the sum of the concentrations of cases (1) and (2) and two characteristic measured curves are also presented. Ch-1 was obtained during an oxidation experiment with Prot. 1 at 575°C/22% O₂ and Ch-2 was obtained at room temperature after changing the gas from N₂ to 4.5% O₂/N₂ in both chambers. The concen-

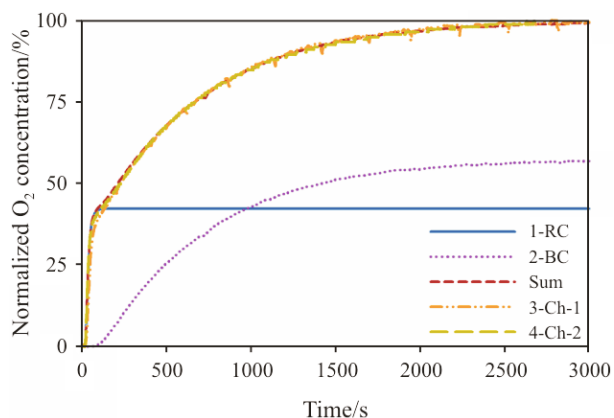


Fig. 5 Normalized O₂ concentration evolution at the TG outlet after changing the gas from N₂ to 22% O₂/N₂: 1 – only in the reaction chamber (RC), 2 – only in the balance chamber (BC), 3 – in both chambers at 575°C (Ch-1) and 4 – in both chambers using 4.5% O₂/N₂ (Ch-2). The composite curve of cases (1) and (2) is also presented (Sum)

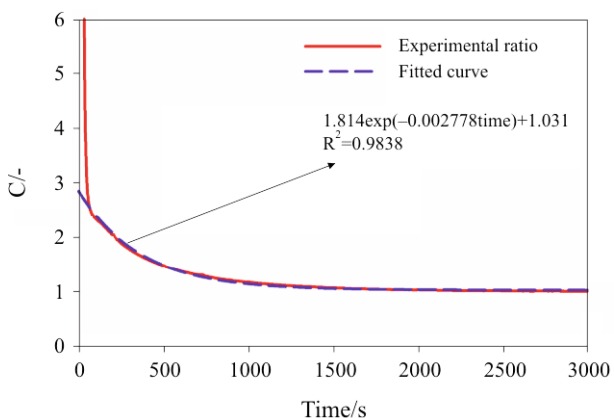


Fig. 6 Ratio (C) of the O_{2,nominal} over the O_{2,current} concentration vs. time

tration data are normalized with respect to the nominal concentration of the gas.

In case (1) the final concentration value is reached in approximately one min after the valve change indicating that the gas change in the sample compartment occurs almost instantaneously. On the other hand, when 22% O₂/N₂ gas flows only through the balance chamber, more than 2000 s are necessary for the O₂ concentration to reach its final value. This may be primarily attributed to the size (Fig. 1) of the balance compartment. The composite curve (sum) simulates accurately the two characteristic measured curves (Ch-1 and Ch-2). As expected, the slower change of the balance gas is imposing its profile leading to not constant concentration in the reaction chamber for over 2000 s after the valve change. The concentration evolution was found to be repeatable whatever the sample compartment temperature and nominal gas concentration.

If O_{2,nominal} is the final nominal concentration of the purge gas used and O_{2,current} is the corresponding running value measured at every instant after the valve change, then the ratio of the two values can be defined ($C=O_{2,nominal}/O_{2,current}$). In Fig. 6 C vs. time is shown for the ‘sum’ curve presented in Fig. 5. Excluding the first 40 s, this ratio can be fitted by an exponential curve, also presented in the graph. The necessity of this ratio becomes clear in the following section.

Comparison and correlation of the two isothermal protocols

The assumption often made in literature [e.g. 13, 14] is made that the global soot oxidation rate measured by TG can be described by a 1st order kinetic equation with respect to sample mass:

$$\frac{dm}{dt} = A \exp\left(-\frac{E}{RT}\right) m [O_2]^n \quad (2)$$

where m is the running sample mass, n is the reaction order with respect to O₂, E is the effective activation energy, A is the effective pre-exponential factor, T is the temperature, t is the time and R is the universal gas constant.

Figure 7 presents the reaction rate r ($r=dm/dt$) and rate constant k ($k=[1/m][dm/dt]$) as functions of α ($\alpha=1-m/m_0$) measured using the two protocols at 600°C/22% O₂ for Printex U. As observed, k determined with Prot. 2 is constant and independent of α in the range 0.1–0.85, while for the measurement with Prot. 1 it is constantly increasing. Furthermore, as expected, the values of r and k measured with Prot. 1 are systematically lower than those measured with Prot. 2, because less O₂ is available for the reaction. For Printex U, at $\alpha=0.5$ with Prot.1 k is found 0.098, 0.16 and 0.26 min⁻¹

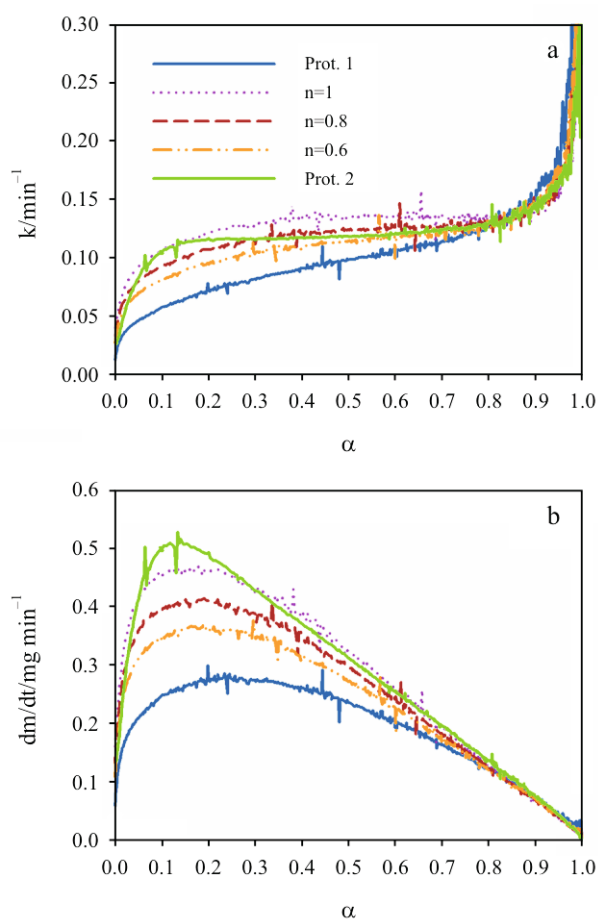


Fig. 7 Measured and corrected $a-k$ and $b-r$ values for Printex U oxidation at $600^{\circ}\text{C}/22\% \text{O}_2$

at 600, 625 and 650°C , respectively, while the corresponding values measured with Prot. 2 were 0.12, 0.24 and 0.4, showing an underestimation of up to 35% of k values with Prot. 1. For diesel soot the corresponding differences are not as high reaching approximately 10%, indicating that the dependence of its reactivity on O_2 is not as strong as for Printex U.

For reactions at the same temperature but at different O_2 concentration, Eq. (2) gives:

$$k_1 = \frac{1}{m} \frac{dm}{dt} = A \exp\left[-\frac{E}{RT}\right] [\text{O}_2]_1^n \quad (3)$$

$$k_2 = \frac{1}{m} \frac{dm}{dt} = A \exp\left[-\frac{E}{RT}\right] [\text{O}_2]_2^n \quad (4)$$

Hence:

$$\frac{k_1}{k_2} = \frac{[\text{O}_2]_1^n}{[\text{O}_2]_2^n} = \left(\frac{[\text{O}_2]_1}{[\text{O}_2]_2}\right)^n \quad (5)$$

Equation (5) states that if k is measured isothermally at a known O_2 concentration, e.g. $[\text{O}_2]_1$, it is possible to calculate k at another concentration, e.g.

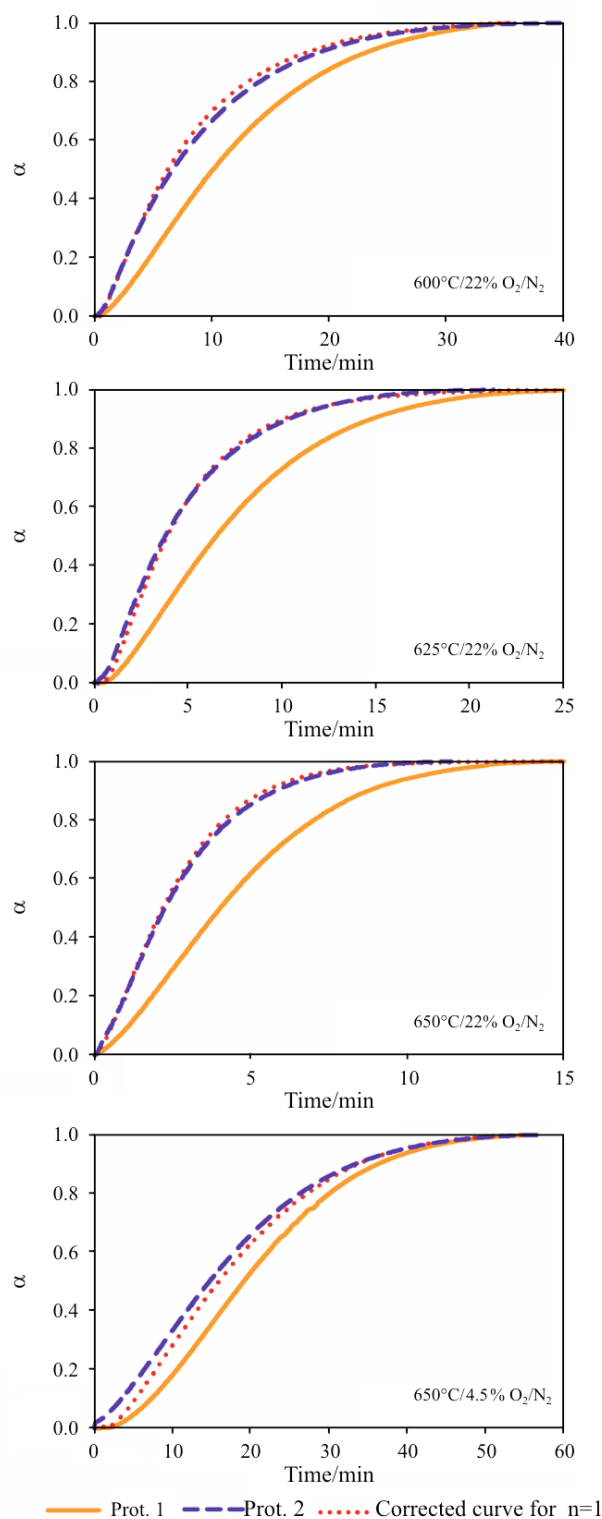


Fig. 8 Measured and corrected α -time curves for the Printex U experiments

$[\text{O}_2]_2$. Let k_2 be the k measured at every instant with Prot. 1 at a variable over time O_2 concentration ($[\text{O}_2]_2$) and ($[\text{O}_2]_1$) be the desired constant concentration used with Prot. 2. Using Eq. (5) it is possible to

correct the values measured under not constant concentration (Prot. 1) with respect to the desired constant concentration. The ratio $[O_2]_1/[O_2]_2$ is defined by the exponential function calculated in Fig. 6.

Using the corrected k values and the integrated form of Eq. (2) it is possible to construct the corrected mass and α -time curves. These must be similar to the corresponding curves obtained with Prot. 2 since they refer to the same O_2 concentration and thus the proposed correction methodology can be validated. The corrected r values result also from these curves.

Until now no assumption was made for the reaction order n with respect to O_2 . Equation (5) was applied to the reaction rates measured with Prot. 1 assuming 3 different n in the range proposed in the literature (0.6–0.8–1) for soot oxidation. The results are

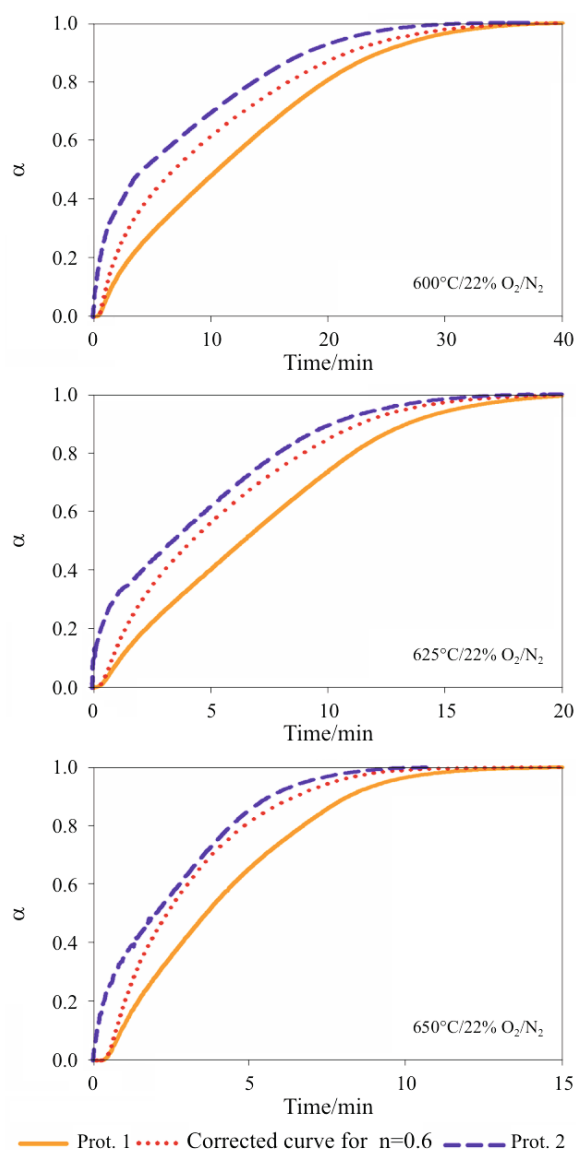


Fig. 9 Measured and corrected α -time curves for the diesel soot experiments

plotted in Fig. 7 together with the values measured with both protocols for Printex U oxidation at $600^\circ\text{C}/22\% O_2$. It is observed that with a proper estimation of n , reliable corrected k and r values can be provided. Both $n=1$ and $n=0.8$ can be used to correct k while $n=1$ gives better correlation for r . Hence, it was decided to use $n=1$ for Printex U. Similarly, $n=0.6$ was chosen for the diesel soot samples.

Figures 8 and 9 present the measured and corrected α -time curves for Printex U and, soot respectively. For Printex U the corresponding curves are almost identical. For diesel soot very similar tendencies are observed for the greater part of the experiments, but the corrected curves have a time shift. This shift may be attributed to the fact that the soot samples used contain approximately 20% volatiles, which are removed very fast after their introduction in the heated furnace. This results in a very steep mass loss in the first 60 s of the reaction. This is not observed with Prot. 1 because these species desorb from the sample during heat-up. It is therefore considered that the above presented methodology can be used successfully for the correction of kinetic data determined with Prot. 1 under various experimental conditions for both samples.

Conclusions

The features of isothermal soot oxidation with intermediate gas change in a Perkin-Elmer TGA6 thermogravimetric analyzer were studied. For this purpose a gas analysis setup involving a conventional analyzer and dilution of the evolved gases was used. This setup was validated showing very good consistency between the initial sample mass calculated via the carbon balance and the one measured directly with the TG.

A protocol including heating up the sample to the reaction temperature in inert atmosphere and then introducing the reactant gas was used (Prot. 1). This protocol is common in soot oxidation studies, because it combines pre-treatment and oxidation of the sample in one run. In addition the balance is allowed to stabilize before the beginning of the reaction and the sample remains in a controlled environment during the whole experiment.

Dedicated tests of the TGA6 balance and reaction gas flows, however, showed that complete change of the gas flowing through the instrument takes up to 2000 s independently of the sample chamber temperature and the O_2 concentration of the reactive gas. To overcome this instrument related deficiency in the application of Prot. 1, a second protocol was used as a reference. In this case the empty furnace was heated up under the reactant gas. The sample was then introduced in the TG at reaction temperature to avoid its partial or total reaction during heat up (Prot. 2).

It was found that Prot. 1 leads to a systematic underestimation of the oxidation rates (up to 35% for Printex U and up to 10% for diesel soot) with respect to Prot. 2. A correction function including the ratio of the reaction gas nominal and current O₂ concentration and the reaction order with respect to O₂ was defined. With this function and an appropriate choice of n it was possible to correct the rates measured with Prot. 1. This was verified through the similarity of the corrected α -time curves with the corresponding curves obtained with Prot. 2. $n=1$ and $n=0.6$ were chosen for Printex U and soot respectively. Since the gas change pattern is characteristic of the instrument this correction function is considered generally valid. Consequently, the developed principle allows the use of Prot. 1 and utilization of its advantages for detailed isothermal soot oxidation studies in the Perkin-Elmer TGA6. Such a study is in progress in our laboratory and its results are expected to be included in an upcoming publication on this matter.

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