

Thermal Characterization of Smoke Composition

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ABSTRACT

The present work includes the thermal characterization of a smoke composition, the smoke components, as well as a potassium chlorate–lactose mixture using differential scanning calorimetry (DSC), thermogravimetry (TG), simultaneous thermogravimetry-differential thermal analysis-Fourier transform infrared spectrometry-mass spectrometry (TG-DTA-FTIR-MS), and accelerating rate calorimetry (ARC).

The DSC results for the smoke composition show a sharp exotherm at 140–210 °C, and the ARC results show one rapid exotherm with an onset temperature of 118 ± 5 °C. These exotherms result from the rapid and energetic reaction between lactose and potassium chlorate. Kinetic studies conducted separately in heat-wait-search and isothermal experiments in the ARC yielded substantially different results for the activation energy. Simultaneous TG-DTA-FTIR-MS was used to investigate the thermal behavior of the smoke composition and to analyze the evolved gases during the heating process. Carbon dioxide (CO₂), water vapour and carbon monoxide (CO) were detected with a significant intensity using FTIR-MS.

Further DSC and TG work was performed for 1-aminoanthraquinone (1-AAQ), a dye that is the main component of the smoke composition. DSC and TG results for the 1-AAQ dye are compared with those for a high purity 1-AAQ dye from a different source. The DSC and TG results indicate that the 1-AAQ dye sample had a significant nonvolatile residual mass compared to the high purity one.

Keywords: smoke composition, orange dye, aminoanthraquinone, thermal analysis, DSC, TG, DTA, FTIR, MS, ARC

Introduction

Pyrotechnic smokes have been widely used for signaling, screening and display. Coloured smokes are preferred, to assure contrast and to be distinct in the presence of clouds and ordinary smoke. The smoke compositions typically contain potassium chlorate as the oxidizer, lactose as the fuel, polyvinyl acetate as a binder, sodium bicarbonate as a neutralizer or cooling agent, and of course the organic dye for colour.^[1] Anthraquinone dyes are commonly used in coloured dye mixes prepared for signal smoke grenades because of their resistance to decomposition by heat and their capacity to evaporate and recondense as a brilliant cloud or trail.^[2]

A smoke composition containing 1-aminoanthraquinone (1-AAQ) dye (orange dye), supplied from Batch 0219 (B0219), was thermally analyzed. The thermal properties for the smoke composition, the 1-AAQ dye, as well as the potassium chlorate–lactose mixture were determined using various techniques, including differential scanning calorimetry (DSC), thermogravimetry (TG), simultaneous thermogravimetry-differential thermal analysis-Fourier transform infrared spectrometry-mass spectrometry (TG-DTA-FTIR-MS), and accelerating rate calorimetry (ARC). Since this particular smoke composition performs well in actual use, its thermal characteristics are a bench mark for future compositions containing components from new batches.

Experimental

Materials

A smoke composition containing: 1-AAQ dye from B0219 (55.0 %), potassium chlorate (21.9 %) and lactose (15.6 %) (the mass ratio of potassium chlorate to lactose is 1.4:1) and samples of each component were provided by Hands Fireworks. A sample of high purity 1-AAQ from Bayer Chemical Co. was also used. Also, a mixture of potassium chlorate and lactose was prepared in our laboratory in the ratio of 1.4:1, respectively.

DSC

A TA 5200 Thermal Analysis System with a DSC 2910 module was used for the thermal studies of smoke composition and the organic dyes in a nitrogen atmosphere. A heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ up to $600\text{ }^{\circ}\text{C}$ was applied to 3.0 mg of the organic dye samples as well as a 1.0 mg sample of the smoke composition. DSC measurements were conducted on dyes loaded into aluminum hermetic pans. The smoke composition was loaded into sealed glass microampoules, as described in the literature.^[3]

TG

A TA 5200 Thermal Analysis System with a TG 2950 module was used to study the smoke composition sample as well as the 1-AAQ dyes (B0219 and Bayer). All samples were heated from room temperature to $1000\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C min}^{-1}$. A platinum pan containing 1.0 mg of the sample was used. The samples were purged with nitrogen or air at a flow rate of $40\text{ cm}^3\text{ min}^{-1}$ to the balance and $60\text{ cm}^3\text{ min}^{-1}$ to the furnace. A TG run with an empty platinum pan (i.e., no sample) showed a deviation from the baseline of approximately $\pm 40\text{ }\mu\text{g}$ up to $1000\text{ }^{\circ}\text{C}$.

TG-DTA-FTIR-MS

The simultaneous TG-DTA 2960 module interfaced to a Bomem MB100 Fourier Transform Infrared Spectrometer (FTIR), and a Balzers Thermostar GSD300 Quadrupole Mass Spectrometer (MS) was used to study the thermal behaviour and to identify the gases evolved during the heating of the smoke composition sample. Experiments were conducted in helium and

air atmospheres purged at a flow rate of $50\text{ cm}^3\text{ min}^{-1}$. Platinum foil was used as a reference material. Approximately 1.0 mg of smoke composition and 1.0 mg of potassium chlorate-lactose mixture were tested using the TG-DTA. An equivalent mass of the sample and a platinum foil were placed in separate alumina pans and heated at $20\text{ }^{\circ}\text{C min}^{-1}$ up to $1400\text{ }^{\circ}\text{C}$. To confirm the baseline of the TG-DTA, an experiment using the same heating profile was performed on two empty alumina pans. The TG drift was $\sim 33\text{ }\mu\text{g}$ ($\sim 3.3\text{ }\%$ for a 1.0 mg sample) and the DTA curve fluctuated less than $0.15\text{ }^{\circ}\text{C}$ over the entire temperature range.

ARC

The ARC is a commercial automated adiabatic calorimeter distributed by Arthur D. Little Inc. and is used for the purpose of assessing the thermal hazards of energetic materials.^[4] About 0.5 g of the smoke composition was placed in a lightweight spherical titanium vessel, which formed part of a closed system including a pressure transducer. Experiments were started at ambient air pressure. The standard ARC procedure of "heat-wait-search" was used: the temperature of the system was raised from the initial temperature of $100\text{ }^{\circ}\text{C}$ in $5\text{ }^{\circ}\text{C}$ steps. The system was maintained adiabatic, both during periods of "wait" for dissipation of thermal transients and of "search" for an exotherm defined as a self heating rate exceeding $0.02\text{ }^{\circ}\text{C min}^{-1}$. The criteria set for the instrument to terminate a run were (i) a temperature maximum of $350\text{ }^{\circ}\text{C}$, (ii) a self-heating rate exceeding $2\text{ }^{\circ}\text{C min}^{-1}$ or (iii) a pressure exceeding 7 MPa (1000 psi). Isothermal runs were performed on 0.5 g of the smoke composition sample and were carried out at 100, 105, 110 and $115\text{ }^{\circ}\text{C}$. The instrument was maintained isothermal for a period of time until onset and a runaway reaction was reached.

Results

Orange Dyes (1-AAQ)

The TG results for the 1-AAQ (B0219) dye and the sample from Bayer, both in nitrogen, are compared in Figure 1. The results indicate that B0219 dye has a significant nonvolatile residual mass (10 %), compared to about 1.3 % for Bayer, independent of the purge gas used in

the experiment. First step mass losses of about 90 % for B0219 and 98.7 % for Bayer were obtained between 150 and 250 °C, resulting from the sublimation of the 1-AAQ dyes. A second mass loss took place for B0219 dye at temperatures higher than 250 °C.

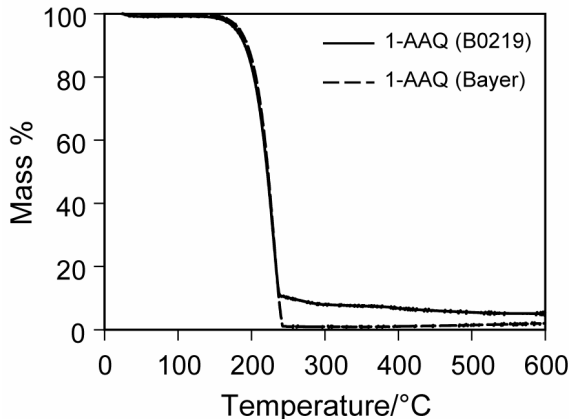


Figure 1. TG curves for two samples of 1-AAQ dye in N_2 at 5 °C min^{-1} .

The DSC results for the 1-AAQ dye (B0219) in an aluminum hermetic pan show one endotherm with an onset temperature of $251.6 \pm 0.2\text{ °C}$ and $\Delta H = 106.9 \pm 0.3\text{ J g}^{-1}$, while the DSC results for the Bayer dye show one endotherm with an onset temperature of $253.0 \pm 0.2\text{ °C}$ and $\Delta H = 112.9 \pm 0.1\text{ J g}^{-1}$. It was observed that the melting point of B0219 dye is a few degrees below that of the Bayer material, indicating the presence of impurities in B0219. For comparison, the reported melting point of 1-AAQ dye is 252 °C and its ΔH value is $127.0 \pm 2.9\text{ J g}^{-1}$.^[5]

Potassium Chlorate–Lactose Mixture

Figure 2 shows the TG-DTA curves for the potassium chlorate-lactose mixture. The DTA curve shows a small endotherm with an onset temperature of about 145 °C , due to the dehydration of lactose monohydrate. The first broad exotherm shows multiple peaks with an onset temperature of about 196 °C . This exotherm may be due to a reaction between potassium chlorate and lactose as well as the exothermic decomposition of lactose.^[6] The TG curve in Figure 2 shows a first-step mass loss of 3 % accompanying the small endotherm, followed by a second-

step mass loss of about 52 % accompanying the first exotherm.

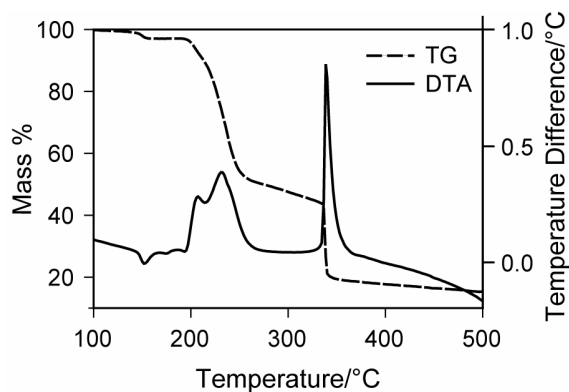


Figure 2. TG-DTA curves for 1.0 mg of potassium chlorate-lactose mixture in He at 20 °C min^{-1} .

A second, sharp exotherm in the DTA curve, with a smaller area than the first exotherm, started at about 336 °C , very close to the melting point of potassium chlorate. This exotherm may be due to further oxidation of residual carbon with potassium chlorate.^[6] The mass loss accompanying this exotherm was about 33 %.

Smoke Composition

Figure 3 presents the DSC and TG results for the smoke composition. A mass loss of about 60% occurred between 140 and 250 °C. By comparing the TG results for the 1-AAQ dye, the potassium chlorate-lactose mixture, and the smoke composition, this mass loss is believed to be due to the dehydration of lactose monohydrate, the lactose-potassium chlorate reaction and the sublimation of the 1-AAQ dye.

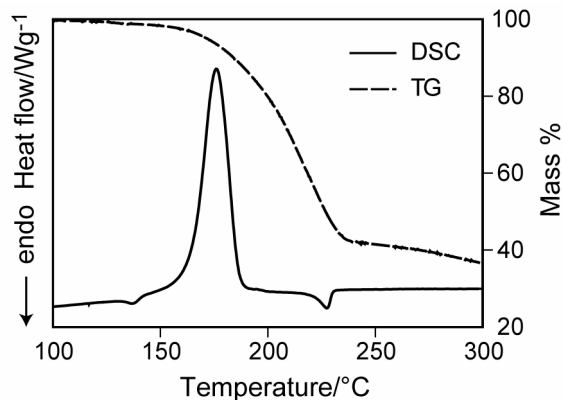


Figure 3. DSC (in ampoule) and TG (in open pan) curves for 1.0 mg of smoke composition in N_2 at $5^\circ C\ min^{-1}$.

A small endotherm observed between 130 and 140 °C is due to the loss of one molecule of water of crystallization from the lactose molecule, which is in agreement with literature results.^[6,7] Subsequently, a sharp exotherm was seen for the composition, due to the rapid and energetic reaction between lactose and potassium chlorate at 140–210 °C with an onset temperature of $142 \pm 1^\circ C$ and $\Delta H = 3.2 \pm 0.1\ kJ\ g^{-1}$ (mass of potassium chlorate and lactose mixture). A small endotherm was observed between 212 and 235 °C resulting from the melting of the 1-AAQ dye.

The ARC results, showing the behaviour of the smoke composition in air, are presented in Figure 4. The smoke composition sample exhibited one exotherm with an onset temperature of $118 \pm 5^\circ C$. As shown in Figure 4, the smoke composition sample displayed continuous exothermic activity that was eventually terminated when it reached a self-heating rate of $2^\circ C\ min^{-1}$.

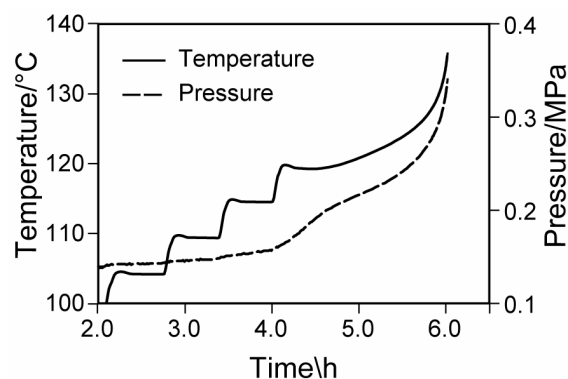


Figure 4. ARC results for 0.5 g of smoke composition in air at ambient pressure.

Figure 5 presents a plot of $\ln(\text{Rate})$ versus reciprocal temperature for the heat-wait-search runs, from which the kinetic parameters of the smoke composition sample were determined. It was found that $E = 298 \pm 10\ kJ\ mol^{-1}$ and $\ln(Z/\text{min}^{-1}) = 88 \pm 1$, where E is the activation energy and Z is the pre-exponential factor in the Arrhenius equation. A value of -3.2 was obtained for $\ln(k/\text{min}^{-1})$ at 120 °C, where k is the reaction rate constant calculated using the kinetic parameters.

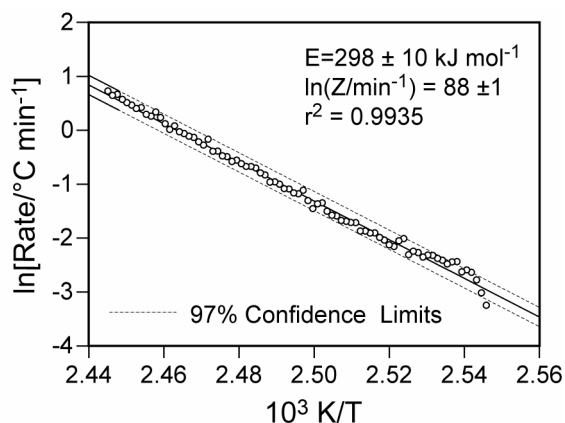


Figure 5. ARC results for 0.5 g of smoke composition in air ($\ln(\text{Rate})$ vs. $1/T$).

Isothermal ARC runs in air at 100, 105, 110 and 115 °C were also performed for the smoke composition. Figure 6 shows a plot of $\ln(\Delta t)$ against the isothermal temperatures, where Δt is calculated as the time taken to reach the maximum rate ($2^\circ C\ min^{-1}$). Assuming a zero order

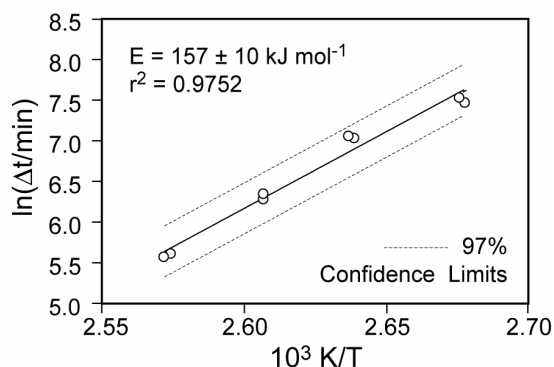


Figure 6. Kinetic results obtained from isothermal ARC data, Δt is time to Rate = $2\text{ }^{\circ}\text{C min}^{-1}$.

reaction, $E = 157 \pm 10\text{ kJ mol}^{-1}$ and $\ln(Z/\text{min}^{-1}) = 43 \pm 3$ were determined from Figure 6. A value of $\ln(k(120\text{ }^{\circ}\text{C})/\text{min}^{-1}) = -5.0$ was obtained.

There is a significant difference between the rate constant and the kinetic parameters determined from the isothermal and heat-wait-search experiments. These differences may result from the invalidity of the assumption of a zero order reaction.

Figure 7 presents TG-DTA results for the smoke composition in both helium and air. In helium, the DTA curve shows a small endotherm between 130 and 170 $^{\circ}\text{C}$, due to the loss of one molecule of water of crystallization from lactose monohydrate, followed by exothermic peaks obtained at onset temperatures of 190 and 300 $^{\circ}\text{C}$, respectively. A small endotherm was observed between those two exotherms. The DTA curve in air shows broader multiple exotherms instead of the sharp one observed in helium. Some of these exotherms can be attributed to the oxidation of the organic dye and other smoke components as the evolution of CO_2 and some water accompanies them in both helium and air (as discussed later with reference to Figures 8 and 9).

A first-step mass loss of about 63 % in helium and 41.5 % in air ends at about 275 $^{\circ}\text{C}$ as shown in the TGA curve in Figure 7. It is possible that some oxidation causing mass increase occurs in the presence of air. Several mass loss steps follow at temperatures $\geq 275\text{ }^{\circ}\text{C}$, where a relatively high residual mass of smoke sample in air was detected compared with that observed in helium. The TGA baseline drift (3.3 %) can, at least in part, be attributed to the loss of moisture from the alumina pan.

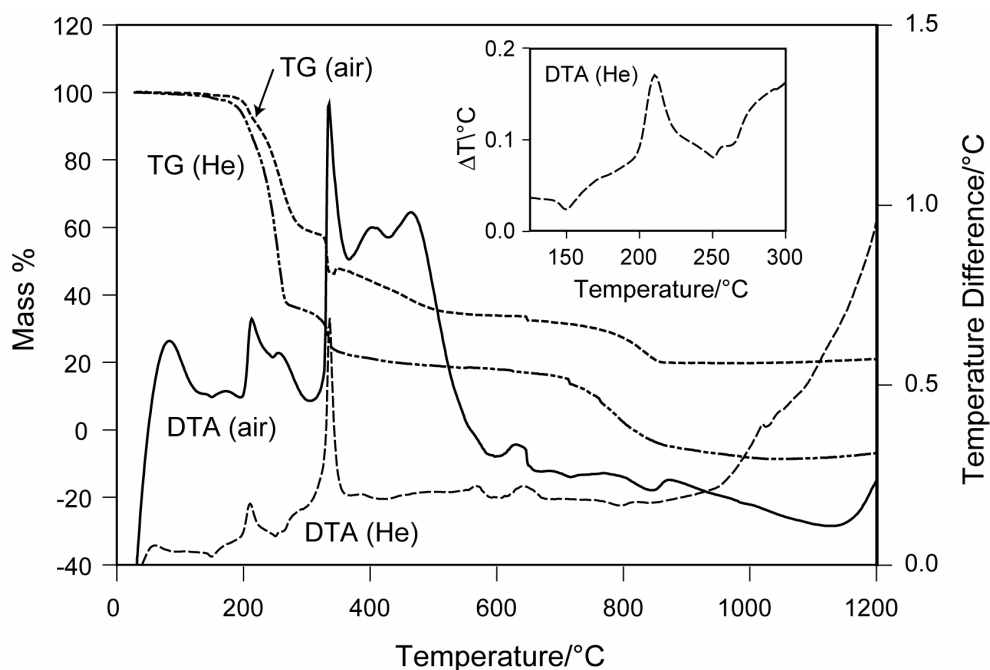


Figure 7. Comparison of TG-DTA results for 1.0 mg of smoke composition in He and in air at $20\text{ }^{\circ}\text{C min}^{-1}$.

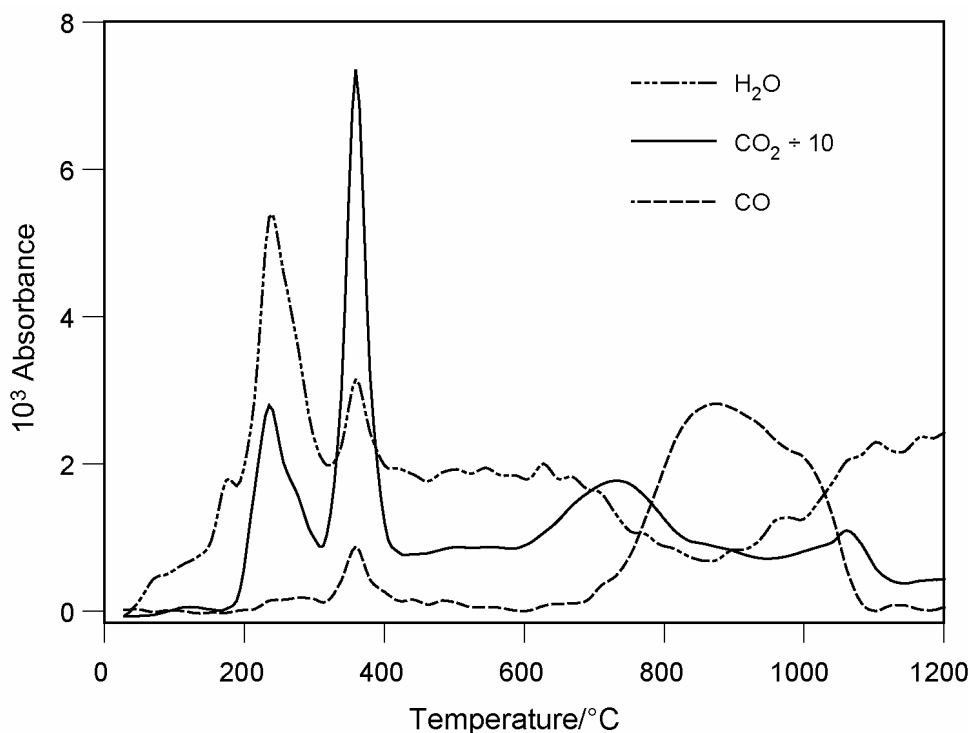


Figure 8. FTIR results for 1.0 g of smoke composition in He at 20 °C min⁻¹.

Figure 8 shows the major evolved gases for the smoke composition in helium. Traces of acetic acid, nitric acid, formic acid and ammonia were also identified by comparing the observed spectra with those provided in a product library.

The detected absorbances of CO₂ and CO were converted to concentration relative to CO₂ (as shown in Figure 9) using scaling factors provided in reference 8. Since the scaling factor for water was not available, its relative concentration was not estimated. The FTIR results in helium (Figure 9) showed that CO₂ was evolved in larger amounts than CO at temperatures below 700 °C, while CO was evolved in larger amounts than CO₂ above 700 °C. In air, CO₂ was evolved in larger amounts than CO over the entire temperature range.

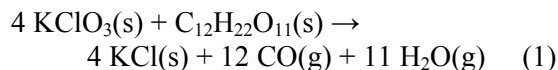
Discussion of Results

Thermal analysis for the smoke composition, the 1-AAQ dyes (from B0219 and Bayer), and the potassium chlorate–lactose mixture was performed using TG, DSC, ARC, and TG-DTA-

FTIR-MS. It was of interest to study the thermal behaviour of components in order to clarify the thermal behaviour of the smoke composition.

According to the TG and DSC results, 1-AAQ dye from B0219 contains a significant amount of nonvolatile impurities, much more than the sample from Bayer.

Heat generated by the reaction of potassium chlorate (oxidizer) and lactose (fuel) is responsible for volatilizing the organic dye in a smoke device.^[1] The smoke composition sample studied in this report was claimed to have a ratio of 1.4:1 by mass (potassium chlorate:lactose). Thus, the potassium chlorate–lactose reaction can be represented by the stoichiometric reaction in equation 1



The DSC, ARC and TG-DTA results show that the smoke composition sample exhibited a smooth and rapid exotherm resulting from the potassium chlorate–lactose reaction (eq 1). This reaction provides the energy that is necessary to cause the sublimation and partial decomposition

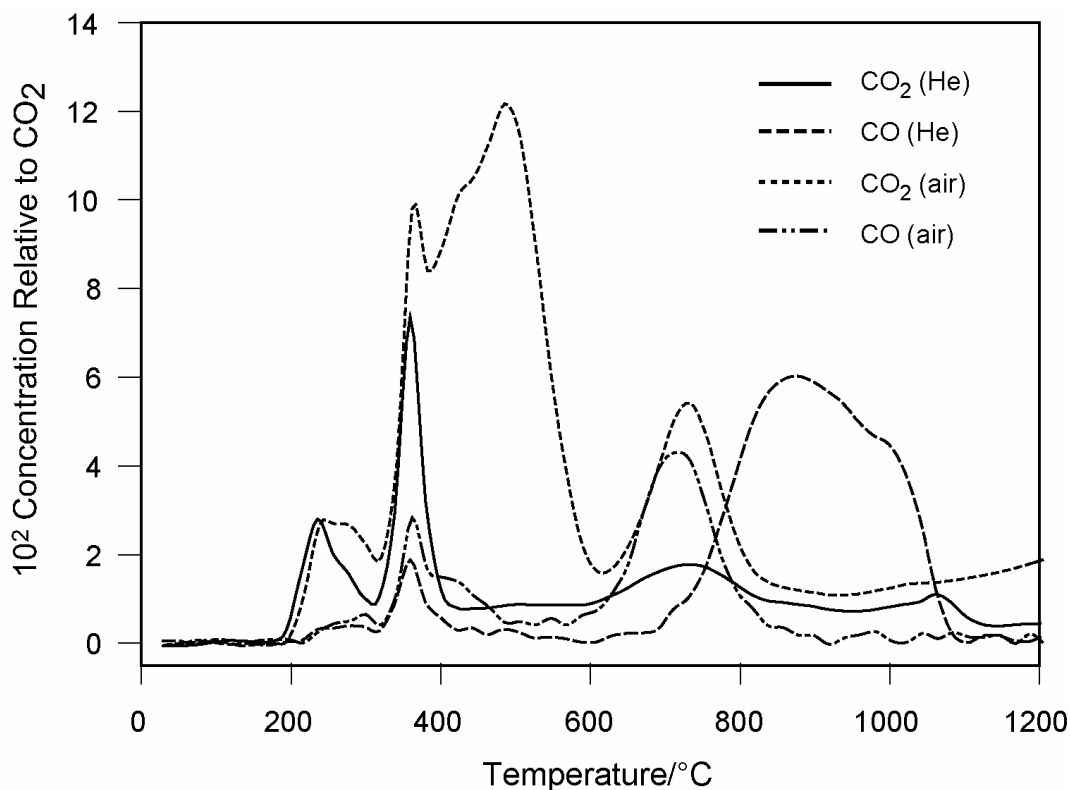
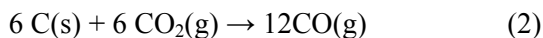


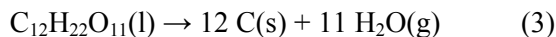
Figure 9. Comparison of FTIR results for smoke composition in He and in air at $20\text{ }^{\circ}\text{C min}^{-1}$.

(an undesirable event) of the organic dye. As shown in the balanced equation 1, CO would be the main product of the reaction. However, FTIR results showed that more CO_2 was evolved than CO for $T < 700\text{ }^{\circ}\text{C}$ (see Figure 9). The production of CO is only favoured above $700\text{ }^{\circ}\text{C}$ as in equation 2:^[9]

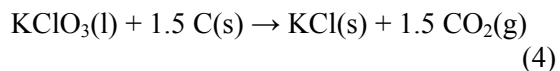


The DTA results suggest that the lactose monohydrate loses one molecule of water between 130 and $170\text{ }^{\circ}\text{C}$ as shown by a small endotherm. Subsequently, a strong exothermic reaction took place at about $200\text{ }^{\circ}\text{C}$, during which some of the potassium chlorate was rapidly reduced to potassium chloride as shown in equation 1. This agrees with TG-DTA results for the potassium chlorate–lactose mixture presented in Figure 2. The temperature of the reaction coincides with that for the fusion of lactose. It may be reasonably surmised that this reaction was initiated by the partial solution of the potassium chlorate in liquid lactose, since potassium chlorate is very soluble in solvents containing hydroxyl groups.^[6] It is likely that the reaction

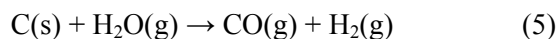
presented in equation 1 occurs simultaneously with the decomposition of lactose between 260 and $300\text{ }^{\circ}\text{C}$,^[6] as shown by equation 3:



This assumption also explains the termination of the reaction before all the chlorate is decomposed, but there is no evidence for this phenomenon in Figure 7. Heat evolved from the reaction presented in equation 1 should be enough to enhance dye sublimation, as shown by a small endotherm at about $240\text{ }^{\circ}\text{C}$ (Figure 7). However, it should be noted that the sample was subjected to a temperature ramp in the experiments and that sublimation of the dye would occur even in the absence of self-heating. The second sharp exotherm (Figure 7), similar to the second exotherm obtained from the potassium chlorate–lactose mixture (Figure 2), occurred between 300 and $370\text{ }^{\circ}\text{C}$, near the melting point of potassium chlorate and this may be initiated by this melting. This reaction is the oxidation of the carbonaceous residues by the remaining potassium chlorate^[6] as presented in equation 4.



The carbonaceous residues might come from residual unsublimed dye, unreacted lactose, the decomposition of polyvinyl acetate or the decomposition of an impurity. In contrast with the first exotherm, less water was evolved (see Figure 8) and the main gaseous product of this reaction was CO_2 as determined by FTIR and MS. It should be noted that the vaporization of the dye occurs before the second stage of the process (200–250 °C) comprising the reactions represented by equations 1 and 4. Several decomposition steps of smoke components were present at temperatures above 500 °C, producing water, acetic acid, nitric acid, formic acid and ammonia as detected by FTIR (Figures 8 and 9). The presence of nitrogen-containing species indicates some decomposition of 1-AAQ. A relatively large amount of CO was produced above 700 °C apparently from the reaction of residual carbon with water (eq 5) or CO_2 (eq 2) or both



The TG-DTA results for the potassium chlorate–lactose mixture of 1.4:1 by mass ratio were compared with those obtained from the smoke composition in Table 1. The peak area (A) is used only for a qualitative comparison and is not an absolute value of enthalpy. The values of A for the smoke composition were calculated as per the mass of potassium chlorate–lactose present in the smoke composition according to the ratio mentioned earlier. In Table 1, the small endotherm is of similar area and onset temperature for the two samples. The first exothermic peak was larger for the potassium chlorate–lactose mixture than that for the smoke composition, which indicates that dye evaporation reduced the net exotherm. The lower value of A

for the smoke composition reflects the fact that a significant amount of the 1-AAQ dye evaporated. The second exothermic peak (see Table 1) was larger for the smoke composition, which indicates the presence of more carbon to be oxidized by potassium chlorate. This carbon might have arisen from unreacted lactose or also from unevaporated dye or from both. The percentage contribution of the potassium chlorate–lactose reaction in the first-step mass loss in the smoke composition was estimated to be about 20 %, based on TG-DTA results for the potassium chlorate–lactose mixture. Assuming similar behaviour of potassium chlorate–lactose mixture in the smoke composition, this means that only 78 % of the dye content in the smoke composition will evaporate.

The smoke composition behaved differently in the TG-DTA and TG with respect to the residual mass content at the end of the runs. These differences may have resulted from the different experimental parameters used in the TG-DTA system compared with those used in the TG, or they may simply have been a result of a lack of homogeneity in the smoke composition sample. The lower residual mass content of the smoke sample obtained from the TG-DTA results in helium compared to that in air (Figure 7) indicates that, under these experimental conditions, the smoke composition contained some residues that were not oxidized in the presence of air.

The sharp exotherm for the smoke composition (Figure 3) suggests that the potassium chlorate and lactose reaction was essentially fast and complete. The impurities in B0219 are still of unknown composition. TG results showed that these impurities are of a nonvolatile nature. They might catalyze the potassium chlorate–lactose reaction, help to conduct heat into unreacted

Table 1. Comparison of TG-DTA Results in Helium.

Sample	Endotherm		1 st Exotherm		2 nd Exotherm	
	T_{onset} °C	$\frac{A}{\text{°C min mg}^{-1}}$	T_{onset} °C	$\frac{A}{\text{°C min mg}^{-1}}$	T_{onset} °C	$\frac{A}{\text{°C min mg}^{-1}}$
Potassium chlorate-lactose mixture	147	0.037	196	0.84	336	0.51
Smoke containing B0219 dye	141	0.034	200	0.19	328	1.08

materials, react with chlorate and supply more heat to the process or some combination of these. An important factor that should be considered is the potassium chlorate to lactose ratio. Any change in this ratio will affect the amount of the dye sublimated due to changes in the heat evolved from the lactose oxidation reaction.

The heat evolved from the exothermic peak for the smoke composition sample of $3.2 \pm 0.1 \text{ kJ g}^{-1}$ (mass of potassium chlorate and lactose mixture), due to the potassium chlorate–lactose reaction, was compared with the literature value of 2.7 kJ g^{-1} for the reaction represented by equation 1. It should be mentioned that it is not expected to get exact ΔH values since the smoke composition is a complex mixture. Although the smoke composition containing B0219 dye functioned well in a smoke device and exhibited a sharp exotherm, it does not necessarily mean that the potassium chlorate–lactose reaction was complete. Smoke compositions are heterogeneous mixtures of a variety of components. Sampling of these mixtures at the milligram scale for DSC/DTA and TG measurements is always subject to uncertainties since these samples may not be representative of the composition on a bulk scale.^[10]

Conclusions

Simple thermal analysis by DSC testing showed that the melting point of 1-AAQ dye from B0219 was lower than that of Bayer, and TG showed that B0219 has a substantial residual mass; both observations point to the presence of an impurity.

The smoke composition reacted smoothly in the DSC and TG-DTA (in helium) experiments showing rapid exotherms and also displaying a smooth, uninterrupted runaway reaction in the ARC.

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