

Study of condition-dependent decomposition reactions Part I. The thermal behaviour and decomposition of 2-nitrobenzoyl chloride

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Abstract

The risks associated with batch processing in the manufacture of chemicals and pharmaceuticals via highly exothermic reactions are of special interest due to the possibility of runaway reactions. *o*-Nitrated benzoyl chlorides are intermediates in the production of agrochemicals and are produced via the reaction of *o*-nitrated carboxylic acids with thionyl chloride in a solvent mixture. *ortho*-Nitrated acyl chlorides have exploded violently on attempted distillation on numerous occasions. An inadequate investigation of the process prior to large-scale operation is the most likely cause. Here we present preliminary results of studies on the decomposition of 2-nitrobenzoyl chloride. This study has revealed that the decomposition reaction is strongly condition dependent. The heating rate of the sample plays a preponderant role in the course of the decomposition reaction. That renders the interpretation of differential scanning calorimetry (DSC) or adiabatic calorimetry measurements, which are routinely used to assess the thermochemistry and safety of the large-scale reactions, problematic. Following this on-going study, we report here key features of the system that have been identified.

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1. Introduction

Runaway reactions arising from the decomposition of thermally unstable materials are a concern in industry due to the potentially devastating effects that they yield. Over the years, as companies have competed to produce a more diverse range of materials using cheaper and faster processes, the need for assessment of these risks has become increasingly more important. Studies into the occurrence of thermal runaway incidents have shown the most likely cause to be a result of an inadequate investigation of the process prior to its operation on a large scale. Knowledge of the reaction chemistry and reaction thermochemistry is very important if a reliable kinetic model is to be established. Other causes include incorrect plant design, scale up, inadequately investigated plant modifications and operator error as shown by Barton and Rogers [1].

o-Nitrated benzoyl chlorides are industrially important intermediates in the production of agrochemicals. They are manufactured from their corresponding *o*-nitrated carboxylic acid by a chlorinating reagent, most commonly, thionyl chloride in the presence of a catalyst and in a mixture of solvents. Dimethyl formamide is usually the catalyst of choice. Several incidents have been reported in association with this family of reactions where aromatic acyl halides containing the nitro group adjacent to the halide function have violently exploded due to thermal decomposition. Two incidents occurred in the attempted distillation of 2-nitrobenzoyl chloride [2,3]. Following the preparation of 2-nitro-3-methylbenzoyl chloride from the corresponding carboxylic acid and thionyl chloride, attempts to distil the compound also led to detonation [4]. In the preparation of 2-nitrobenzoyl cyanide from 3-methoxy-2-nitrobenzoyl chloride an explosion resulted on heating the mixture to 60 °C [5]. This finding was attributed to the well-documented instability of *o*-nitrated acid chlorides as reported by Bretherick [6]. Incidents describing the thermal decomposition of such compounds are encountered in the literature. However, the kinetics and mechanism of

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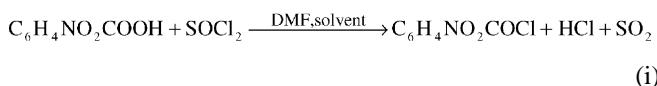
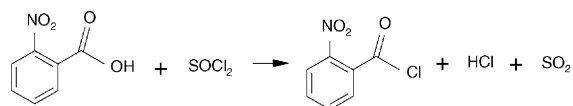
the decomposition and the nature of the decomposition products are not documented. The effect of water, moisture and air on the thermal stability of the *o*-nitrated benzoyl chlorides is one of the primary stages in a thermal hazard assessment. The lack of information available prevents a selection of process operating conditions that would prevent a thermal runaway.

It is the purpose of this study to gain an understanding of the kinetics and mechanisms involved in the decomposition of *o*-nitrated benzoyl chlorides. Here we present the methodology that has been followed in preliminary studies on the decomposition of 2-nitrobenzoyl chloride. As a result of those studies a new design that enables the power output profile of the decomposition to be determined and the measurement of gas production from the decomposition to be measured in different environments, is now underway.

2. Background chemistry

The chlorination of nitrated carboxylic acids is an important reaction in the field of agrochemical and fine chemical industries. The chlorinated products are important intermediates. However, they are thermally unstable and the safety of the process has to be carefully studied. Here we present the first results of a project that targets their thermal study.

2-Nitrobenzoyl chloride is produced by the *o*-chlorination of 2-nitrobenzoic acid using thionyl chloride (synthesis reaction). *N,N*-Dimethylformamide is commonly the catalyst of choice and the reaction has been carried out in various solvents and solvent mixtures. Hydrogen chloride and sulphur dioxide are produced by the synthesis reaction. The reaction proceeds by the following stoichiometry:

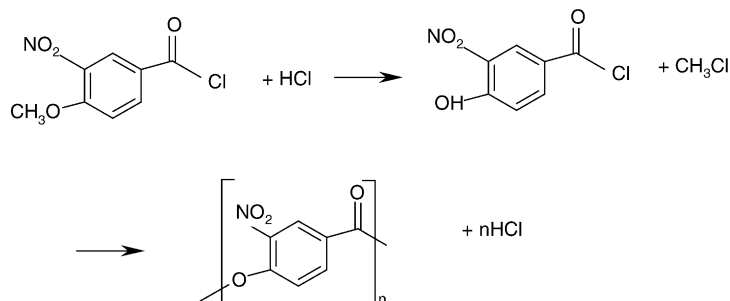


The thermal effects of the synthesis reaction depend on the conditions under which it is performed due to the sig-

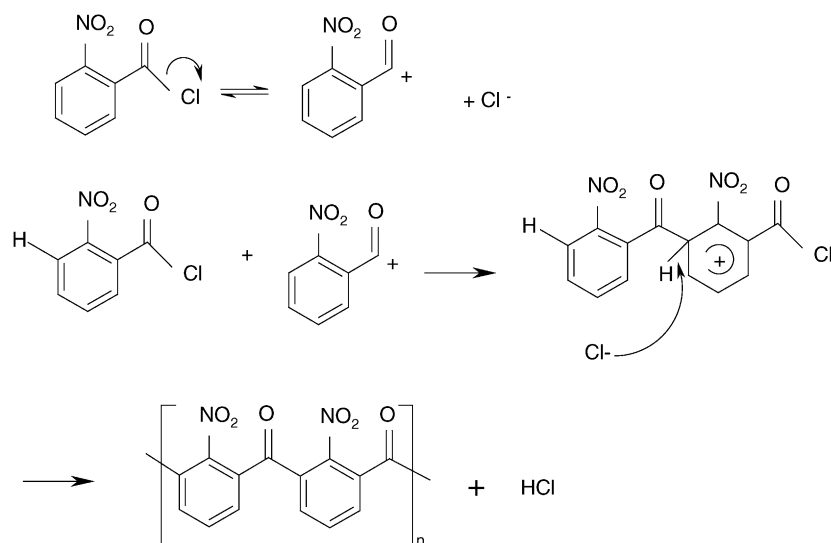
nificant heat of solution of the produced gases. In a closed system, where escape of gases is not possible, the process is exothermic, while, in an open system due to the escape of the produced gases the process is endothermic. The solubility of the gases obviously depends on temperature, but also, as found in our previous research [7] on whether these gases are individually or jointly equilibrated with the solvents. This induces significant complication in the assessment of the release of power in case of a reaction runaway. The behaviour of this synthesis reaction has been previously reported by Bosshard et al. [8] and is beyond the scope of this paper. However the manufacturing process and operating conditions should be kept in mind to enable the effects, if any, on the thermal stability of the product to be considered when studying its decomposition and evaluating potential runaway scenarios.

The kinetics and mechanism of the decomposition of *o*-nitrated acid chlorides have not been studied. In many cases, the products of thermal decompositions are unknown and are frequently polymers varying in length and composition. If information is available regarding the decomposition of organic compounds having the same functional groups then the initial assumption is that their decompositions follow the same path. In a previous incident [9] during the manufacture of 4-methoxy-3-nitrobenzoyl chloride from 3-nitro-4-methoxybenzoic acid and thionyl chloride, the reaction mass was held at 100 °C for 4 h. When the gas evolution had terminated a double explosion occurred. Further studies revealed that the decomposition of the acid chloride occurred in two stages. HCl dimethylates the acid chloride to generate methyl chloride and the hydroxyacyl chloride. Condensation of the hydroxyacyl chloride generates the polynitro phenyl carboxylic ester and HCl. Further dimethylation can then occur by the HCl produced. The second decomposition is attributed to the NO₂ group. A schematic for the formation of the polynitroester is shown in Scheme 1.

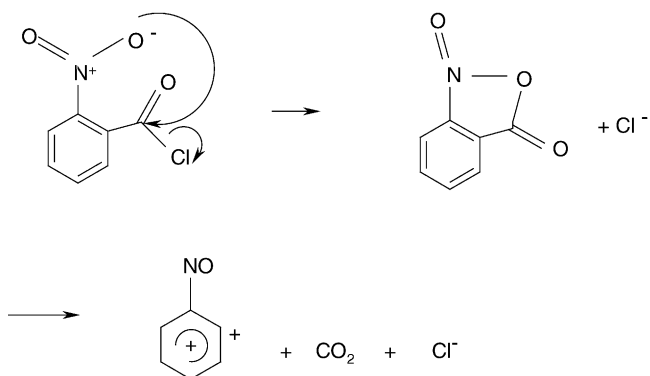
With regard to the decomposition of 2-nitrobenzoyl chloride a number of potential intermediates, which in most cases are expected to act as monomers that contribute to the formation of polymers and co-polymers are shown in Schemes 1–10. They have been considered in the product analyses as explained later.



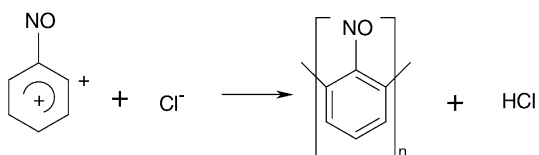
Scheme 1. Decomposition of 3-nitro-4-methoxy benzoyl chloride during manufacture [9].



Scheme 2. Decomposition of 2-nitrobenzoyl chloride to form poly(2-nitrobenzyl-3-ketone) [10].



Scheme 3. Generation of nitrosobenzene ion, carbon dioxide and a chlorine ion [11].



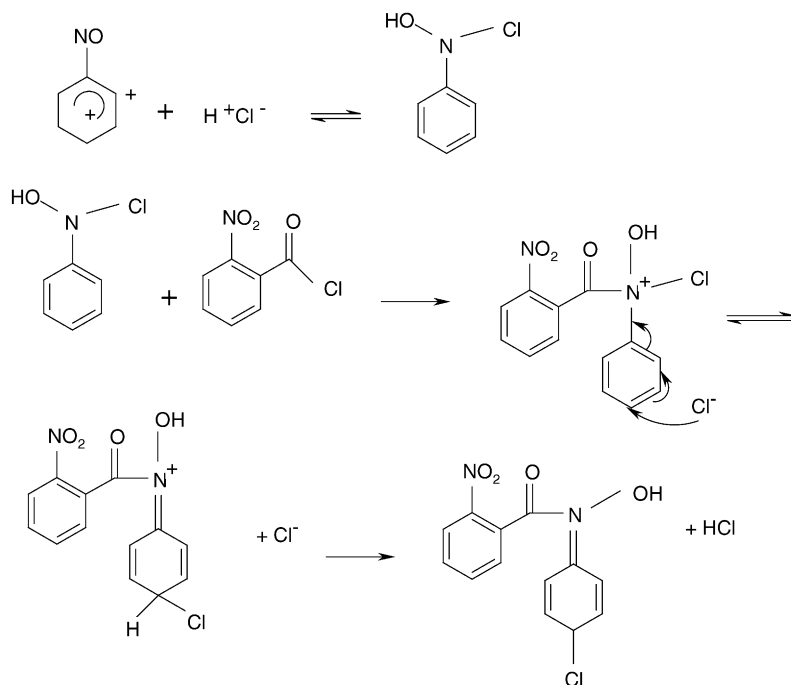
Scheme 4. Formation of polynitrosobenzene [11].

3. Experimental

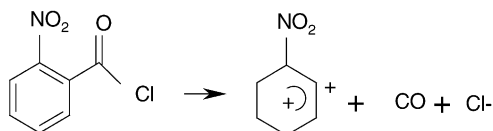
The decomposition of 2-nitrobenzoyl chloride (Fluka 73100) was studied under different conditions. Experiments were performed using a number of different quantities of samples, in an open vessel in air and in an inert environment. During preliminary tests, a known mass of 2-nitrobenzoyl chloride was heated in a furnace. A 4.8 cm diameter borosilicate glass reactor was placed in a 5 cm bore, 26 cm long cylindrical furnace. The sample was placed in a small diameter cylindrical glass holder, which was coaxially sintered inside the borosilicate glass reactor. A type K thermocouple

fixed to the wall of this sample holder, very close to the sample, was used for the temperature measurements. The geometry of the reactor and the sample holder was such that the sample was positioned at the hottest part of the furnace, which also maintained a uniform temperature. A Eurotherm 91e temperature controller controlled the power supply, which heated the furnace to the desired temperature. The only means of cooling the system was via heat losses. A schematic of the furnace is shown in Fig. 1.

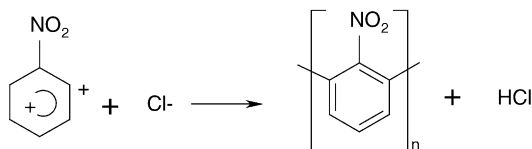
Initially, a substantial mass of 2-nitrobenzoyl chloride (approximately 7 g) was heated slowly, over a period of several hours, so that its temperature was increased linearly from ambient to 600 °C in order to determine the apparent onset temperature of exothermic decomposition and the gas evolution. It was found that the decomposition initiates at approximately 170 °C and that it is accompanied by a substantial heat and gas generation. The product of the first decomposition, a tar looking solid, was subsequently completely mineralised at around 500 °C in an open system in the presence of air. This article focuses on the first stage of decomposition, namely the one initiating at around 170 °C. Following the identification of the “onset” of the decomposition, subsequent measurements employed a much reduced sample quantity. The furnace containing the reactor was set to a constant temperature, which was gradually lowered from one measurement to the next in order to slow-down the decomposition reaction and identify the best isothermal conditions for its study. Similar trials were carried out with constant sample heating using varying heating rates. A second methodology involved a simple set up of a small very wide flask containing a film of sample heated by a hotplate. A PTFE insulated thermocouple was held in the sample to monitor continuously the sample temperature throughout the measurement. In every measurement the gas flow-rate was measured using a bubble flow-meter and also by weighing the amount of silicon oil which was displaced by the gas,



Scheme 5. Formation of nitrosobenzene in the decomposition reacts with acid chlorides to produce the corresponding *N*-*p*-chlorophenylhydroxamic acid. The presence of HCl catalyses the reaction [12].



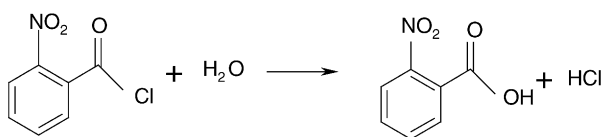
Scheme 6. Decomposition to produce nitrobenzene ion, carbon monoxide and Cl^- .



Scheme 7. Formation of polynitrobenzene.

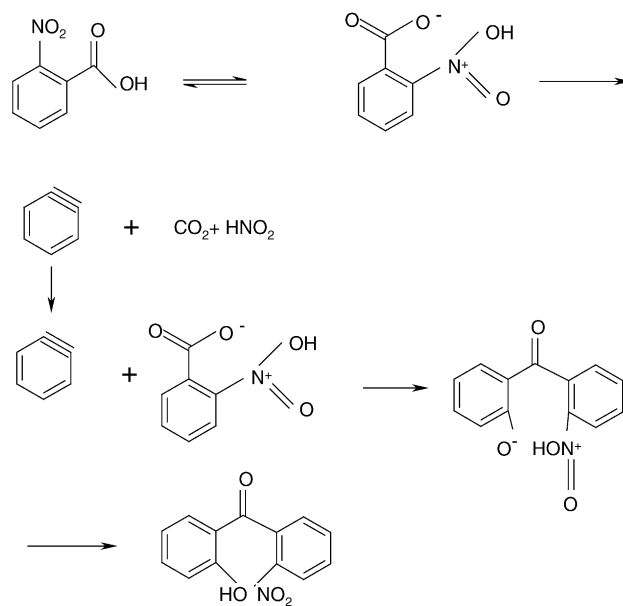
a measurement which also provided the total gas evolution due to the decomposition. Experiments were carried out in air and in argon to determine the effect, if any, on the gases produced by the decomposition. Product gases were collected in silver nitrate solution to verify the production of hydrogen chloride gas.

During the decomposition samples of the product gases were taken and analysed by gas chromatograph with a TCD

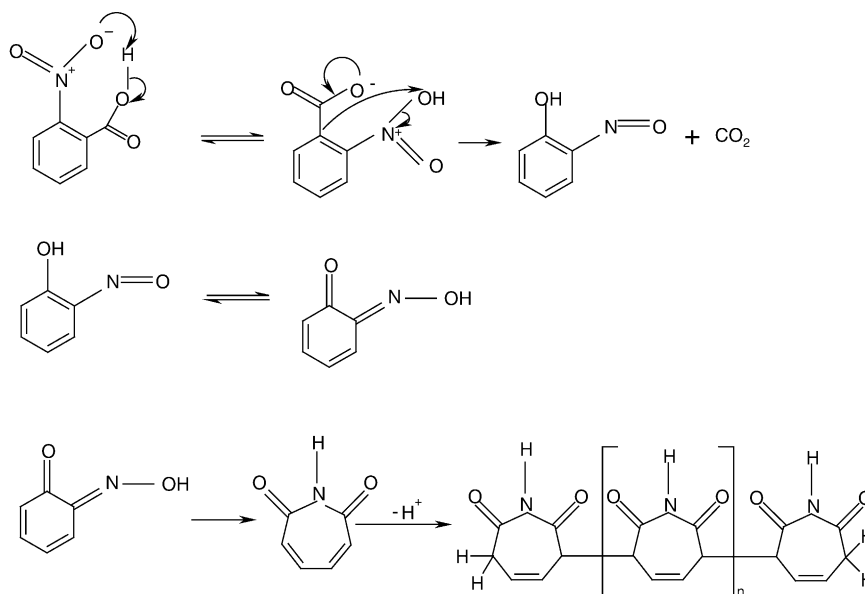


Scheme 8. Initial reaction of 2-nitrobenzoyl chloride with water (if present in the system).

for characterisation. Further analyses were carried out to examine the effects of the conditions under which the decomposition proceeds on the composition of the sample residue. Samples were taken following a rapid non-isothermal decomposition and a slow near isothermal decomposition. In all cases, the decomposition products were held at an elevated temperature following the apparent completion of the decomposition, for several hours. Samples of the solid



Scheme 9. Decomposition of the carboxylic acid formed to 2-nitro-2'-hydroxybenzophenone [13].



Scheme 10. Decomposition of 2-nitrobenzoic acid and subsequent decomposition of nitrosophenol [13].

residue were taken immediately after the decomposition appeared to have finished and then following the hold period. They were analysed by mass spectroscopy (MS) (reported accuracy 5 ppm) using fast atom bombardment (FAB) and electro spray (ES) techniques. Three instruments were used; FAB +ve VG Autospec (Sector Instrument), ES +ve Micromass LCT and ZMT Electro spray. A Carlo Erba Elemental Analyser 1108 was used to determine the percent C, H, N content of the solid residues (accuracy $\pm 0.3\%$). Oxygen flash combustion followed by titration with mercuric nitrate was used in the quantification of percent Cl contained in the sample. It was observed that the decomposition products strongly depend on the heating rate and on the environment that the decomposition takes place. A more sophisticated ex-

perimental set up for the study of this reaction is currently being tested.

4. Results and discussion

4.1. Measurements of the temperature history and the gas production

Fig. 2 shows the temperature rise caused by three samples of different mass. In all cases the furnace temperature was maintained constant at approximately 166°C . The temperature profile along the length and diameter of the furnace had previously been tested to ensure that the sample was contained in the area where furnace temperature was uniform. The sample was placed at the hottest part of the furnace, where the temperature was a few degrees higher than the controller set-temperature. In all experiments shown here, the sample was heated to 100°C at $10^\circ\text{C min}^{-1}$ and then at 2°C min^{-1} to the finally desired constant oven temperature.

Table 1 shows the results of five typical measurements performed in the oven, including the ones presented in the graph and two measurements performed in a hot plate. The reported gas production measurements have been corrected for gas thermal expansion. In order to reduce error, the dead volume of the system was minimised. The sample mass used in the hot plate measurements was substantially higher than the mass used in the furnace. Gas samples were collected at regular intervals and analysed in the GC. The content of the samples in carbon dioxide, carbon monoxide, nitrogen, hydrogen and hydrogen chloride was measured. Production of carbon monoxide, carbon dioxide and hydrogen chloride was verified and measured during the reaction. The latter was tested by titration with silver nitrate.

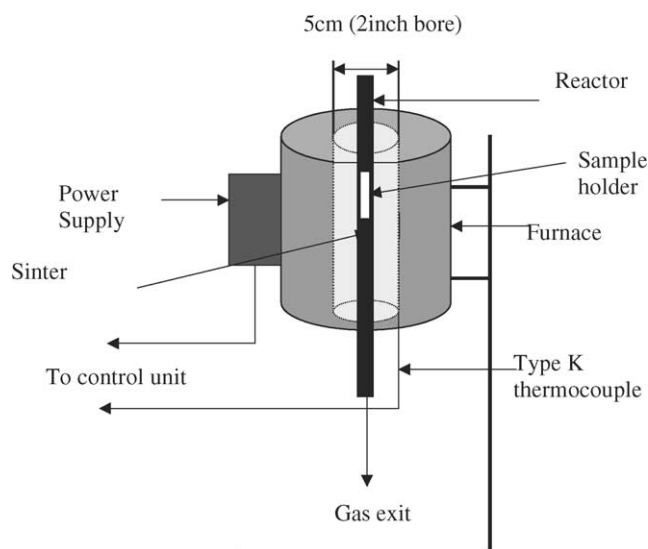


Fig. 1. Schematic of furnace used in preliminary measurements.

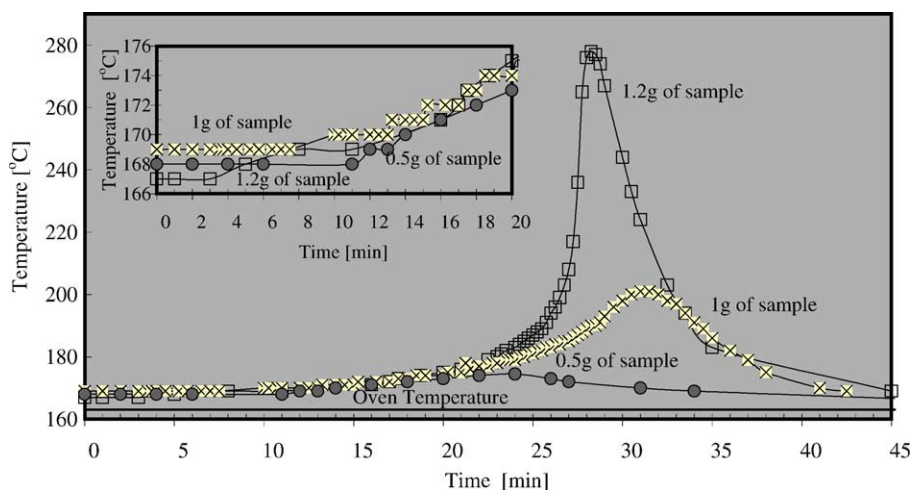


Fig. 2. Temperature profile of the decomposition when 1.2, 1 and 0.5 g of sample was heated to 166 °C and left to decompose: (●) 0.5 g of sample; (×) 1 g of sample; (□) 1.2 g of sample.

Table 1

Summary of the results obtained when samples varying in mass were heated to different starting temperatures

Run no.	Sample mass (g)	Sample temperature at zero time (°C)	Sample temperature rise (°C)	Volume of gas produced (ml)	Apparent time length of decomposition (s)	Graph
Furnace decomposition						
1	1.2010	167	112	–	3000	
2	1.0200	167	33	27	2500	X
3	0.5075	168	5	3	1750	O
4	0.5181	167	13	6	1000	–
5	0.99	165	127	50	1000	–
Hot plate decomposition						
6	7.20	165	<5	113	5000	
7	3.20	164	15	92	2300	

Measurements were performed in air and in an inert atmosphere, which was created by purging the system with argon prior to the measurement. Measurements taken using the hotplate were manually controlled to limit the temperature rise due to the exothermic decomposition to the desired level. In those larger scale measurements hydrogen chloride production became apparent at temperatures as low as 120 °C. However reaction did not occur to a measurable extent unless the sample temperature was set above 160 °C. The inert atmosphere did not seem to affect the measurements, but, as mentioned previously, the volume of air in the system was very small, so its influence is yet to be tested. Further experiments are currently underway to examine the influence of different environments. It was found, and it becomes obvious from Tables 1 and 2 and Figs. 3 and 4, that the reaction pathways, manifested by the rate of self-heating and the total, but also the individual, gas production, strongly depend on the sample heating (or self-heating) rate.

Figs. 2–4 show sample results from the decompositions carried out in the furnace using a relatively small amount of sample. The influence of the heating rate on the progress of the decomposition reaction is highlighted in Figs. 3 and 4. It can be seen that for an otherwise identical measurement, a

small difference (of the order of 5 °C) in the sample heating rate—shown more clearly in the embedded graphs—results in a very dissimilar path of decomposition. In both figures, the sample that is heated at a slightly lower rate later decomposes at a much faster rate producing a much more pronounced peak in power and gas generation. This could be due to a slow, untraced decomposition, which has started before the temperature of 165 has been reached, having consumed much of the reactant. The reactant accumulation in the measurement with slower heating rate will thus be less than the reactant accumulation in the sample heated more rapidly. Although, this seems a plausible explanation there is strong evidence from the mass spectra analyses that the heating rate determines the decomposition pathways. Notably

Table 2

Total volume of CO₂, CO and HCl produced by the decomposition when 7.2 g sample was heated on a hotplate

7 g sample	Total gas produced			
	CO ₂	CO	HCl	Total
Volume (l)	0.013	0.002	0.098	0.113
Mole	5.8×10^{-4}	8.9×10^{-5}	4.3×10^{-4}	5.0×10^{-3}

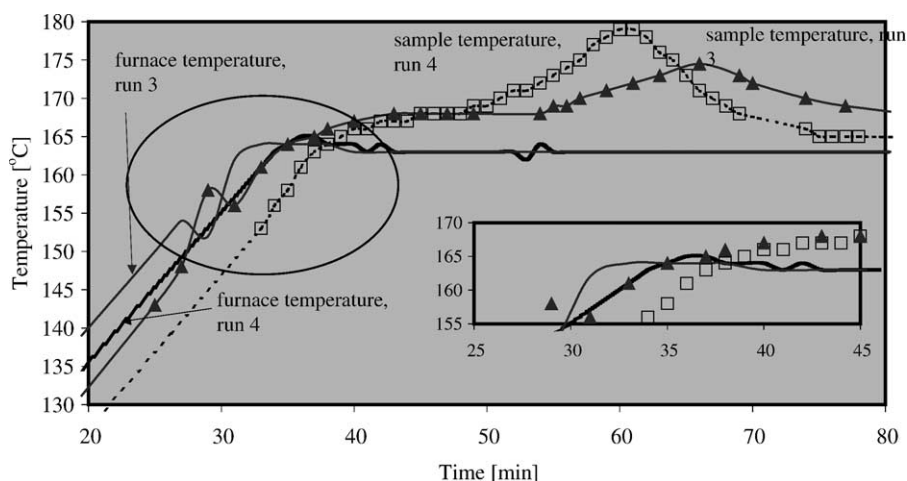


Fig. 3. Sample and furnace temperature for two measurements (runs 3 and 4 in Table 1), performed under the same conditions using 0.5 g samples.

the mass spectra analyses demonstrated that the temperature progression of the decomposition had a marked effect on the products of the decomposition.

4.2. Results and interpretation of solid residue analyses

To gain some insight regarding the reactions taking place, a series of measurements were performed using always the same set up and identical sample-masses but different heating rates. Residue samples were analysed immediately after the end of the gas production and 5 h later, having kept the sample at 168 °C for 5 h. Table 3 shows the results of the elemental analyses obtained for two samples of the solid residue one from a near isothermal decomposition and one of a rapid, far from isothermal; decomposition. The obtained compositions are by mass. For comparison purposes, the composition of a number of other molecules is shown in Table 4. Table 3 shows the “molecular formula” of a fictitious substance with the

composition suggested by the elemental analyses shown in Table 3.

The resultant formulae and the results in Tables 3 and 4 show that near isothermal decomposition results in the loss of chlorine only yet upon rapid decomposition, both chlorine and oxygen are lost. The reduced percentage in nitrogen and chlorine in the nearly isothermal decomposition, which is lower than any of the potential monomers shown in Table 4, suggests that substances with zero nitrogen content (e.g. 7 or 8) should be present. Substances with zero content in chlorine (e.g. 1, 3, 4, 6, Table 4), too. Moreover, the relatively high oxygen content also implies that substance 1 should be included. Similarly, substances like 4 and 6, Table 3, high in carbon and low in chlorine were expected to be present in the residue of the fast decomposition. MS, FAB MS, and ES analysis carried out on the product of the decomposition near isothermal and rapid decomposition conditions provided evidence that these assumptions are correct. These analyses have shown that polymers consisting of various proportions

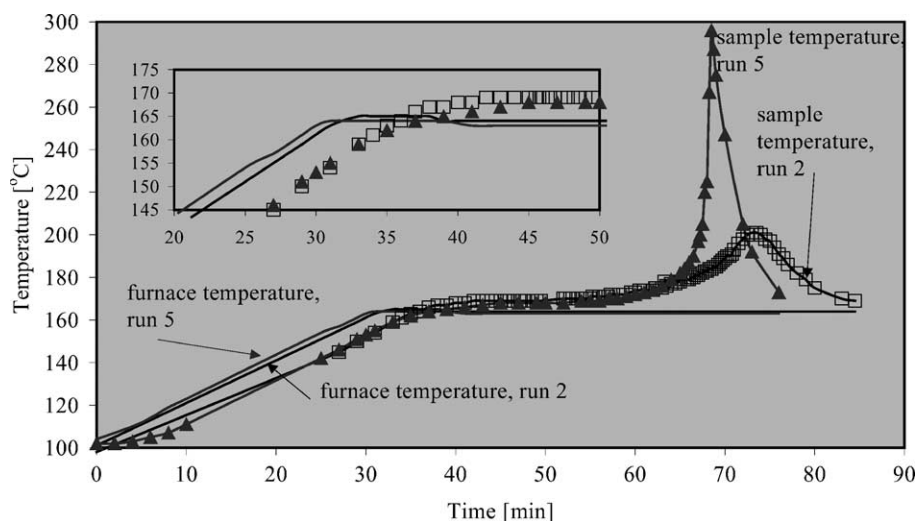
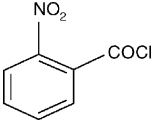


Fig. 4. Sample and furnace temperature for two measurements (runs 2 and 5 in Table 1), performed under the same conditions using 1 g samples.

Table 3

Comparison of elemental analysis results on fast ($\Delta T > 100^\circ\text{C}$) and slow ($\Delta T < 10^\circ\text{C}$) thermal decomposition with unreacted 2-nitrobenzoyl chloride

	Element (%)					Fictitious formula
	C	H	N	O	Cl	
	45.4	2.2	7.6	26	18.9	$\text{C}_{84}\text{H}_{48}\text{N}_{12}\text{O}_{36}\text{Cl}_{12}$
$\Delta T_{\text{dec}} < 10^\circ\text{C}$	48.7	2.5	8.0	29.3	11.35	$\text{C}_{84}\text{H}_{56}\text{N}_{14}\text{O}_{42}\text{Cl}_7$
$\Delta T_{\text{dec}} > 100^\circ\text{C}$	59.7	2.8	10.2	14.87	12.4	$\text{C}_{84}\text{H}_{48}\text{N}_{12}\text{O}_{15}\text{Cl}_6$

of nitrosobenzene, nitrobenzene and 2-nitrobenzyl-3-ketone monomers are produced in addition to polymers made up of the same monomer units, i.e. polynitrosobenzene, polynitrobenzene and poly(2-nitrobenzyl-3-ketone). The terminating groups differed between COCl, COH, Cl and H. In all of the analyses carried out, di(2-nitrobenzyl-3-ketone) with a chlorine terminating group was detected.

The results of the analysis showed that the products of the reaction varied depending on the sample self-heating rate and the temperature attained on decomposition. Where the sample reached a higher temperature on decomposition, the molecular masses of the compounds detected ranged from 100 to 700 g mol^{-1} . Where the decomposition took place at near isothermal conditions, the molecular mass of the compounds detected ranged from 200 to 1000 g mol^{-1} . When the sample was heated moderately fast and held for a period of time at an elevated temperature, compounds ranging in mass from 200 to 2000 g mol^{-1} were detected. However, following well-controlled experimental conditions, very fast decomposition early products (shortly after the end of the gas generation) were identical with those obtained after the prolonged 5h heating that followed. The maximum chain length of the polymers detected in the near isothermal run, moderately rapid and very fast decomposition were 8, 15 and 5, respectively.

Structures were assigned to all molecular masses detected by the analyses and they were consistent with previously reported monomers or products. However, more than one plausible molecular structures could often be assigned to molecules with higher masses, thus their detailed description is not presented here. Their exact form has to be uniquely identified in the future using more sophisticated techniques.

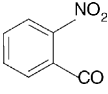
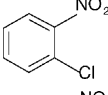
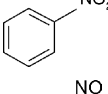
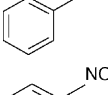
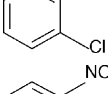
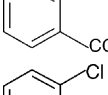
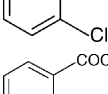
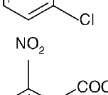
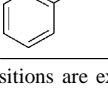
4.3. Qualitative product identification and rationale

Analysis of the compounds produced by near isothermal conditions and those produced by the decomposition where a temperature rise in excess of 100°C was experienced showed in both cases that formation of the 2-nitrobenzyl-3-ketone polymer (Scheme 2) had taken place. In both cases, the $n = 2$ polymer were present in the sample. However, the solid residue of the sample taking place at near isothermal conditions had formed a series of the same polymer where n

= 3–6. In the sample which had experienced a greater temperature rise and decomposed over a shorter time period, higher polymers where $n = 12$ –14 were identified. This can be attributed to the gradual propagation of the polymerisation reaction by the near isothermal decomposition. Where the decomposition is more rapid, the lower polymers are

Table 4

Comparison of the compositions of the initial sample with potential intermediate monomers and products of the decomposition of 2-nitrobenzoyl chloride at very low and very high decomposition rates

No.	Potential products	Element (%)				
		C	H	N	O	Cl
1		56	2.67	9.33	32	0
2		45.86	2.55	8.92	20.38	22.3
3		58.54	4.06	11.38	26.01	0
4		67.29	4.67	13.08	14.95	0
5		51.06	2.84	9.92	11.35	24.82
6		62.22	2.96	10.37	23.70	0
7		49.31	2.74	0	0	47.94
8		48.27	2.29	0	9.19	40.22
9		45.4	2.2	7.6	26	18.9

Compositions are expressed as percent mass.

likely to link together to form higher polymers. This is confirmed by the results of the mass spectra.

The reduced volume of gas produced when the same mass of sample experienced different temperature rises on decomposition is probably due to the consumption of the HCl produced by the decomposition in the formation of poly(2-nitrobenzyl-3-ketone) (Scheme 2). The isothermal decomposition generated 2-nitrobenzyl-3-ketone polymers ranging in length from 2 to 6.

The length of the 2-nitrobenzyl-3-ketone blocks amongst the co-polymers increased in length upon rapid decomposition. Longer chains of 2-nitrobenzyl-3-ketone polymers were detected in the co-polymers of moderately rapid decomposition—an increase from a maximum of 2 monomers units to 8 was shown on moderately rapid decomposition.

The presence of nitrobenzene amongst the co-polymers was not affected by the temperature progression of the decomposition. Higher polymers of nitrobenzene were detected following rapid decomposition.

The heating rate however had a remarkable effect on polynitrosobenzene production. The length of the nitrosobenzene polymer increased from 3 under isothermal conditions to 15 when the sample decomposed at moderate rates and was held at an elevated temperature for several hours. This was also evident in the composition of the co-polymers identified: the presence of nitrosobenzene was more evident in the copolymers formed on rapid decomposition.

The presence of polynitrobenzene and polynitrosobenzene in the products shows that the decompositions shown in Schemes 4 and 5 take place. Where rapid decomposition took place, higher polymers of nitrosobenzene were detected. Larger blocks of nitrosobenzene were detected in the co-polymers formed by the rapid decomposition. These findings suggest that the formation of the nitrosobenzene intermediate is more pronounced at higher temperatures due to the strength of the nitrogen oxygen bond. These findings are confirmed by the results of the elemental analysis where the oxygen content of the sample was found to be significantly reduced by the higher temperatures achieved on rapid decomposition of the sample.

2-Nitrobenzoic acid was detected in only one of the experiments where rapid decomposition took place indicating that the hydrolysis of the acid chloride (Scheme 8) can take place. Products of the decomposition of 2-nitrobenzoic acid encountered by Andreozzi et al. [13] for the decomposition of the carboxylic acid at temperatures above 220 °C (Schemes 9 and 10) were not evident in the analyses carried out in this study, presumably due to the absence of 2-nitrobenzoic acid or due to the lower temperatures employed here. However these suggestions are still relevant for further study into the effects of water on the progress of the decomposition.

The formation of the hydroxamic acid from the reaction of the acid chloride was not apparent in any of the analysis

of the decomposition products. In the reported formation of the hydroxamic acid [12], the reaction takes place in acetonitrile. If the manufacture of the acid chloride takes place in a solvent or solvent mixture containing acetonitrile (which is a quite common approach), the formation of the hydroxamic acid would be more likely to occur.

4.4. Isothermal calorimeter design for further studies

These results of the MS and elemental analysis show that the progress of the decomposition is sensitive to the temperature environment of the sample. This has very important implications for the safe design of large-scale plants. Two systems have thus been designed to enable the decomposition to be studied isothermally, or following a predetermined temperature profile. The low-temperature systems operate as a power compensation reaction calorimeter. It consists of a jacketed 25 ml reactor. High temperature oil is circulated through the vessel jacket. Its inlet and outlet temperatures are measured by Pt(100), platinum resistance thermometers. Isothermal conditions are maintained throughout the decomposition by a power compensation heater and the heat generated by the decomposition is recorded. A Pt(100) platinum resistance thermometer records the temperature of the sample throughout the decomposition. The design allows the decomposition to be carried out in different environments, e.g. air, oxygen, argon and the measurement of gas flow from the decomposition is recorded by a flow-meter. In the study of thermal decompositions, an appreciable sample size is favourable to ensure that the results are as characteristic as possible of a large-scale unit. The equipment, can operate up to 250 °C and has been designed such that appreciable quantities can be studied. It is currently tested. It allows for:

- accurate temperature control;
- measurement of gas production;
- loading of the reactor at elevated temperatures;
- use of a considerable amount of reactant;
- the study of decomposition in different environments, e.g. air, oxygen, argon;
- determination of the power output profile of decomposition; and
- evaluation of the heat of decomposition.

A similar reactor design, which will feature the same as the above characteristics, with cooling and heating facility, able to operate isothermally at higher temperatures (700 °C) is also currently underway.

5. Conclusions

The thermal decomposition of 2-nitrobenzoyl chloride has been investigated. The products of the decomposition, volume of gas produced and heat of reaction were found to vary depending on the sample self-heat rate, heating-rate applied to bring the sample to decomposition temperature and

the maximum temperature obtained by the sample on decomposition. Polynitrosobenzene formation and its presence amongst the co-polymers were increased on rapid decomposition. Higher polymers of 2-nitrobenzyl-3-ketone were also detected following rapid decomposition.

It was revealed that in order to study the kinetics of condition dependent decomposition reactions, like the current one, the reaction has to be extremely well controlled and the samples used for these studies have to be of a substantial size. In view of this, a method has been developed to study the decomposition under isothermal conditions using a power compensation facility. A large mass of sample can be studied to enable the development of a global kinetic model for the decomposition of *o*-nitrated benzoic acid chlorides.

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