Effects of heating rate, temperature and iron catalysis on the thermal behaviour and decompostion of 2-nitrobenzoyl chloride

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Abstract

Runaway reactions arising from the decomposition of thermally unstable materials are a concern in industry due to the potentially devastating effects that they yield. 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. The chlorination of *ortho*-nitrated carboxylic acids is an industrially important reaction in the fine and agrochemical industries. The products of these reactions, *ortho*-nitrated acid chlorides, have been involved in runaway incidents that have resulted in violent explosions; hence, their thermal stability must be studied. Previous studies [S.D. Lever, M. Papadaki, Study of condition-dependent decomposition reactions: the thermal behaviour and decompostion of 2-nitrobenzoyl chloride, Part I, J. Hazard. Mater. 115 (2004) 91–100] showed that the decomposition of the parent molecule, 2-nitrobenzoyl chloride, is highly condition-dependent with the sample heating rate and temperature of decomposition playing a preponderant role in the course of the decomposition. Here, we present the results of studies of the decomposition of 2-nitrobenzoyl chloride, when the sample is subjected to various heating treatments, temperatures and in the presence of iron. As the temperature of decomposition was increased from 150 to 162 °C, the heat of decomposition was reduced from −215 to −90 kJ/mol. As the heat up rate applied in bringing the sample to the decomposition temperature increased, the heat of decomposition also increased. An increase in the heat up rate from 2 to 7.5 °C/min resulted in an increase in the heat of decomposition from −90 to −215 kJ/mol. The presence of iron and silver was observed to lower the heat of decomposition from −185 to −160 and −110 kJ/mol, respectively. Under most conditions investigated, the temperature at which gas flow was initiated was 147–150 °C. The presence of iron reduced this temperature to 140 °C. Decomposition was observed to take place over two stages, where the sample was heated directly from 40 °C at the required heat up rate. Where the sample was heated in stages and where calibrations had been carried out preceding decomposition, the decomposition took place in one stage alone.
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1. Introduction

At some stage in the majority of processes taking place in the chemical industry, a chemical reaction will take place, where initial reactants, solvents and catalysts are mixed under specified conditions to generate the desired product. Prior to the reaction stage of the process, several preparatory phases often take place in addition to unit operations that follow the reaction. Highly exothermic batch processes present a specific hazard due to the possibility of runaway reactions. These

occur if the heat generated by the reaction exceeds the heat dissipation capacity of the cooling equipment and surroundings. Endothermic reactions are not immune to the dangers of thermal runaways. If the products generated by a reaction are thermally unstable, thermal decomposition can be initiated following the main reaction. Possible secondary reactions taking place at all stages in the process must be considered if the safety of the process is to be assured. These factors, coupled with a desire for the most economical and time effective processes, make the assessment of the reactive hazards of a process imperative. Previous thermal runaway incidents have mostly been attributed to an inadequate investigation of a process prior to large-scale operation [2]. Incorrect plant design, scale up, inadequately investigated plant modifications and

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operator error were also cited as the causes of thermal run-aways [2].

Known reaction kinetics (concentration and temperature dependence of the rate of reaction) is a precursor to being able to accurately predict the behaviour of a system in case of a reaction runaway or thermal decomposition. The rate of heat production is directly proportional to the rate of reaction and is determined by calorimetric measurements. Conventionally, isothermal reaction calorimetry in the form of heat flow, isoperibolic or power compensation techniques are used to study the thermal behaviour of the normal reaction whilst adiabatic calorimetry is used to study the behaviour of a system under runaway conditions [3]. In this work, we present the results of an isothermal/isoperibolic calorimetric study of the decomposition of 2-nitrobenzoyl chloride.

The thermal instability of nitrobenzoyl chlorides with the chloride function substituted in the ortho position is well documented. *o*-Nitrobenzoyl chloride, the parent molecule in this family of compounds, is reported to have undergone violent decomposition on attempted distillation [4,5]. Incidents have also been reported during the preparation of 2-nitrobenzoyl cyanide from 3-methoxy-2-nitrobenzoyl chloride [6] and during the attempted distillation of 2-nitro-3-methylbenzoyl chloride following its production from the reaction of the carboxylic acid with thionyl chloride [7]. In industry, *ortho*-nitrated acid chlorides are produced via the chlorination of the corresponding carboxylic acid with a chlorinating reagent in the presence of a catalyst and in a mixture of solvents. They are important intermediates in the fine and agrochemical industry.

To date, the kinetics of the decomposition of 2-nitrobenzoyl chloride has not been studied. In our previous work [1], the decomposition was found to be highly condition-dependent. The heat of decomposition, volume of gas evolved and products of decomposition were found to vary depending on the temperature history of the sample. A methodology was developed that would enable the decomposition to be studied, in what is essentially an isothermal calorimeter, following a predetermined temperature profile. Here, we present the results of the study of the decomposition of 2-nitrobenzoyl chloride, where the thermal treatment of the sample and the final temperature to which the sample is heated differ. The effect of the presence of iron powder and silver on the decomposition has also been investigated. Following on from our previous work, the current study has shown that different reaction paths dominate depending on the conditions under which the decomposition takes place with more emphasis on the thermal effects exhibited by the possible decomposition paths that have already been highlighted.

2. Background

In furnace experiments carried out previously [1], a sample of known mass was heated to an intermediate temperature of 100 °C at a rate of 10 °C/min and then to approximately 160 °C at rates varying from 2 to 3 °C/min. The sample was subsequently left in the furnace at that temperature and allowed to decompose. All of the decompositions were shown to take place in one stage only, yet the duration of the heat up period, over the temperature range 100–160 °C, was found to significantly affect the sample self-heating rate and the maximum temperature reached during decomposition, which was also confirmed by the current study. Analysis of the residues from a near isothermal decomposition and a decomposition, where a temperature rise in excess of 100 °C was experienced by the sample during its decomposition showed that the composition of the residues varied. Detailed mechanisms showing the formation of possible products of decomposition have been previously discussed [1] and are not presented here. In all residues, polymers and co-polymers of nitrobenzyl-3-ketone, nitrobenzene and nitrosobenzene were detected. In comparison to the residue of the near isothermal decomposition, there was marked increase in the formation of polynitrosobenzene following rapid decomposition and its presence amongst the co-polymers was also increased. Higher polymers of nitrobenzyl-3-ketone were detected following rapid decomposition of the sample. The presence of a series of lower ketone polymers following the near isothermal decomposition was probably attributed to the gradual propagation of the polymerisation under isothermal conditions. Nitrobenzene and its presence amongst the co-polymers did not vary with the temperature progression of the sample during decomposition. The low nitrogen content of the sample shown by results of elemental analysis, regardless of the temperature history of the sample, suggested the presence of chlorobenzenes amongst the co-polymers.

The polymerisation (polycondensation) reactions that are apparent from the results of the analysis are Friedel Crafts type reactions [8]. Typically, these reactions are utilised in the manufacture of ketones and involve the reaction of an acyl halide and an aromatic substrate. In theory, *o*-nitrobenzoyl chloride provides both the substrate and the acid chloride necessary for the reaction to proceed and the monomer units of nitrobenzene and nitrosobenzene detected in the product analyses are highly satisfactory substrate molecules. Friedel Crafts synthesis reactions are catalysed by metal halide complexes, most commonly, $AlCl_3$. Metal/iron contamination of the acid chloride would result in the formation of a metal chloride complex that in turn catalyses the formation of the aromatic ketone. Upon decomposition of *o*-nitrobenzoyl chloride, the formation of the aromatic ketone was observed to take place in the absence of metal contamination. This is supported by the literature, where these reactions have been previously reported to take place upon heating alone [9,10].

3. Experimental

The calorimeter employed in the current study is shown in Fig. 1 and is comprised of a small-jacketed borosilicate glass
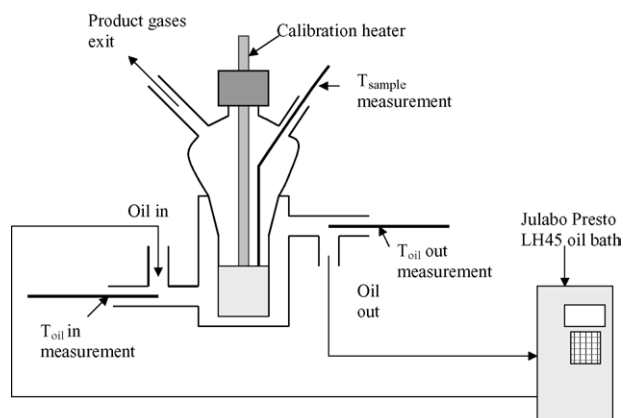
Fig. 1. Schematic of experimental set up employed.

reactor, 25 ml in volume that is agitated with a magnetic stirrer. The calorimeter is also equipped with a calibration heater and a gas measuring facility. Oil is circulated through the reactor jacket from a Julabo Presto LH45 unit. In all of the experiments, the sample was weighed using a balance accurate to 1 mg. Samples in the order of 15 g were employed in the current study. Pt 100 thermometers with an accuracy of 0.1 °C were used for the measurement of the reactor temperature, the oil entering and the oil leaving the jacket. The temperature measurements were performed by a data acquisition system.

Experiments were performed in heat flow isothermal and isoperibolic mode. The power generated by the reaction is calculated according to the following energy balance:

$$\frac{dq_{reaction}}{dt} = \frac{dq_{flow}}{dt} - \frac{dq_{calibration}}{dt} + \frac{dq_{evaporation}}{dt}$$
$$- \frac{dq_{stirring}}{dt} + \frac{dq_{losses}}{dt} + \frac{dq_{accumulation}}{dt} \quad (1)$$

All the terms of the above equation indicate power, as the symbols q and t correspond to heat and time, respectively. The suffices are used to indicate, the power generated by the reaction, the power exchanged with the cooling medium in the jacket, the calibration power, the power loss due to possible evaporation, added power due to stirring, thermal power losses and accumulated power.

The power transferred to the circulating cooling medium is calculated from the following relation:

$$\frac{dq_{flow}}{dt} = UA(T_r - T_j) \quad (2)$$

where U is the heat transfer coefficient between the jacket and the reactor, A the heat transfer area, T_r the temperature of the reactor and T_j is the temperature of the jacket.

The calibration power, $d(q_{calibration})/dt$ is directly measured.

The power loss due to possible evaporation of the reacting mixture was found to be insignificant for the current system.

Power due to stirring and power losses are not normally calculated explicitly but they are included in a baseline. For the calculation of the baseline, UA and the accumulated power ($dq_{accumulation}/dt$), a series of calibrations have been employed. Their calculation was subsequently performed using the methodology presented by Papadaki and Nawada [11].

Initially, a series of calibrations were carried out on an 18.5 g sample to establish a heat transfer model for the system that could be applied in all of the calculations of heat of decomposition. The height of the sample was decreasing as the decomposition proceeded. Calibrations performed to determine the UA coefficient and the heat losses from the sample to the surroundings depend on the area available for heat transfer. It follows from this that throughout the measurements, variations in the height of the sample must be accounted for if a reliable value for the heat transfer coefficient, U, is to be established. During calibrations, two different levels of electrical power were supplied to the sample, where the temperature in the oil bath was set to 40, 80, 110 and 130 °C. Two sets of calibrations at 80 and 110 °C were carried out to ensure repeatability. For experiments taking place using heat flow calorimetry, the system was programmed so that the sample was initially held at 40 °C for 20 min (so that the sample was heated from the same temperature to the required decomposition temperature over a specified time period irrespective of the temperature variations in the laboratory on a day-to-day basis) before being heated at a rate of 2 °C/min up to the required isothermal temperature. Three isothermal experiments were carried out at 150, 153 and 157 °C using approximately 14 g 2-nitrobenzoyl chloride in each run. In isoperibolic experiments, the temperature in the oil bath was held at 40 °C for 20 min and then subjected to a specified heating rate to bring the temperature in the reactor to the required level. Three isoperibolic runs, each employing 14–15 g samples, were carried out using a 2, 3 and 7.5 °C/min initial heat up rate to bring the sample to the required temperature. In two subsequent experiments, the effects of the presence of iron and the effects of calibrations preceding decomposition on the heat of decomposition and the reaction path were studied. Finally, the combined effects of the presence of silver and calibrations prior to decomposition, through the decomposition of the sample from which the heat transfer model had been developed, were investigated. These experiments were carried out isoperibolically.

A Carlo Erba Elemental Analyser 1108 was used to determine the % C, H, N contents of the solid residues. Oxygen flash combustion followed by titration with mercuric nitrate was used in the quantification of % Cl contained in the sample.

4. Results and discussion

4.1. Calibrations

Table 1 shows the results of the calibrations carried out using 18.543 g 2-nitrobenzoyl chloride. Sample height

Table 1
Results of calibrations carried out on an 18.543 g sample before decomposition had taken place

Reactor temperature (°C)	UA	Height (cm)	Area (cm²)	U (W m⁻² K⁻¹)
106.9	0.4969	3.95	29.51	168.39
39.4	0.2461	3.82	28.52	86.29
77.5	0.3454	3.9	29.18	118.38
125.8	0.5618	4.2	29.84	188.28
78	0.3253	3.9	29.18	111.49

measurements taken at the calibration temperatures are also shown in table along with the *UA* values determined and the subsequent calculation of the heat transfer coefficient, *U*. Where calibrations at 110 and 80 °C (oil bath temperature) were repeated, the results were found to be repeatable.

Fig. 2 shows the results of all *UA* values determined by calibrations on 18.543 g sample prior to decomposition and values of *U* calculated. Since the sample mass varies from one experiment to the next, the development of the heat transfer model rests with the heat transfer coefficient *U* rather than the *UA* value. A quadratic has been applied to both sets of data and a quadratic equation is shown for each on the graph, however, *U* data are the most important.

4.2. Effects of temperature

Table 2 shows a summary of experiments 1–4, where the decomposition took place at 150, 153, 157 and 162 °C, respectively. In experiments 1–3, the temperature in the reactor was held at 40 °C initially and then increased to the desired temperature at a rate of 2 °C/min. In experiment 4, the system
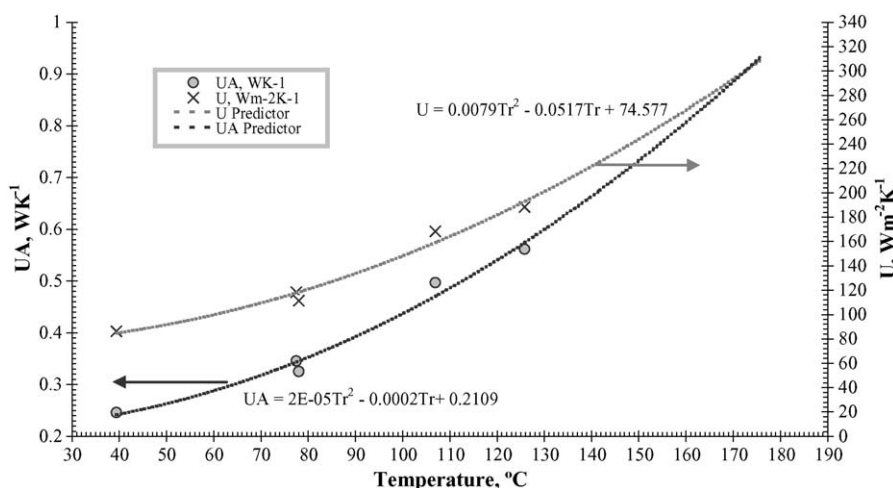

Fig. 2. Development of the heat transfer model to enable prediction of the heat transfer coefficient in all experiments without performing calibrations prior to decomposition.

Table 2
Summary of results obtained when approximately 14 g sample was decomposed at 150, 153, 157 and 162 °C

	Experiment			
	1	2	3	4
Experimental temperature (°C)	150	153	157	162
Sample mass (g)	14.373	14.672	14.495	14.028
Steady-state reactor temperature (°C)	149.7	153.7	157.1	161.4
Mode of operation	HF	HF	HF	IP
Total heat generation (kJ)	16.5	17	15.5	7.5
Heat of decomposition (kJ/mol)	215	200	185	90
Volume of gas produced (ml)	700	650	750	400
Temperature at start of gas flow (°C)	147	147	147	150
Minimum jacket temperature (°C)	148.2	150.3	153.7	161.1
Maximum reactor temperature (HF) or maximum temperature reached during first stage in the decomposition (IP mode)	150.4	153	156.8	164.5
Maximum temperature achieved in second stage of decomposition (°C) (IP mode only)	–	–	–	164.6
Time taken for decomposition to proceed (min)	400	328	287	89
Number of stages of decomposition	One	Two	Two	Two

Samples were heated from 40 °C to the desired temperature at a rate of 2 °C/min. Samples were continuously agitated throughout. No calibrations had been performed prior to decomposition. HF, heat flow mode; IP, isoperibolic mode.
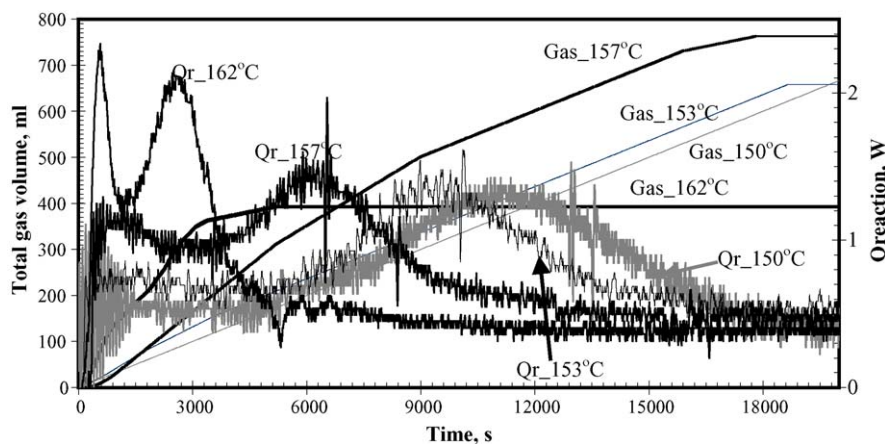
Fig. 3. Power output and cumulative gas production for the decomposition of 2-nitrobenzoyl chloride at 150, 153, 157 and 162 °C. Gas indicates gas production in millilitres and Q_r indicates the power output profile at each temperature.

was operating isoperibolically and the temperature of the oil bath was set to maintain 40 °C for 20 min before heating up at a rate of 2 °C/min to a bath temperature of 167 °C (bath temperature was approximately 5 °C higher than that of the reactor). Fig. 3 shows the temperature and power output profiles for experiments 1–4. In all but the 150 °C measurements, the decomposition is seen to proceed in two stages. The power output profile for the decomposition of the sample at 150 °C shows the decomposition to take place in one stage only. Previous studies carried out on the decomposition of 2-nitrobenzoyl chloride also showed the decomposition taking place in one stage only [1]. In our previous work [1], the sample was initially heated from room temperature to 100 °C at 10 °C/min before the heating rate was adjusted to 2 °C/min and the sample was heated to its final specified temperature. In the current study, the heat up of experiment from 40 to 150 °C at 2 °C/min, was carried out in stages. Moreover, in a number of preliminary experiments (not shown here), where samples were heated up in stages to the decomposition temperature they appeared to decompose in one stage only. These findings show that the decomposition proceeds in two stages when the sample is heated continually from room temperature to the decomposition temperature. However, where the sample is held at a relatively high temperature before being heated to the required temperature for decomposition to take place, the decomposition is observed to take place over one stage alone.

Values of the heat of decomposition have been calculated for experiments 1–4. The total heat output for experiments 1–4 was found to be 16.5, 16.7, 15.4 and 7.4 kJ, respectively. These values correspond to heats of decomposition equivalent to 215, 200, 185 and 90 kJ/mol. These results show that the heat of decomposition decreases with increasing temperature. In experiments 2–4, the first exothermic peak becomes more pronounced with increasing temperature.

Fig. 3 also shows the cumulative gas production during experiments 1–4.

In the three heat flow experiments carried out at 150, 153 and 157 °C, the total volume of gas produced was 700, 650 and 750 ml, respectively. Gas evolution was detected at 147 °C in all three experiments. Upon increasing the decomposition temperature from 157 to 162 °C, the volume of gas produced was approximately halved from 750 to 400 ml and the heat of decomposition was halved from 185 to 90 kJ/mol. At this temperature, gas evolution was not detected until the sample reached 150 °C. The reduced volume of gas when the decomposition was carried out at 162 °C could possibly be attributed to the polymerisation of the chloronitrosobenzene monomer that is endothermic in nature and results in the formation of only one mole of gas (CO_2) as opposed to two.

As the temperature of decomposition is increased, the rate of gas production is seen to increase. During the 150 °C run, the rate of gas production remains constant at approximately 2 ml/min. When the temperature is increased to 153 °C, the initial gas evolution rate reaches 3 ml/min, before it is reduced to 2 ml/min following the first stage of decomposition and continues steady pace until the reaction is complete. The initial rate of gas production in the 157 °C run is 3–4 ml/min. The rate of gas production is reduced during the first stage of decomposition and continues to fall until reaction is complete. In the initial stages of decomposition at 162 °C, the rate of gas evolution reaches 12 ml/min before passing through a minimum at 2 ml/min and increasing again to 10 ml/min. The rate of gas evolution is proportional to the slope of the power output profile of the decomposition. As the rate of heat release in the first exotherm is increased, so too is the rate of gas evolution. Since the rate of heat release is proportional to the rate of reaction, this shows that gas producing polycondensation reactions are taking place at a faster rate at higher temperatures.

Table 3 shows the results of calculations that have been carried out to determine the heat output when suggested monomer intermediates are formed from the initial molecule,

Table 3
Results of calculations to determine the overall heat effects of the decomposition

	Possible formation of intermediate, I, from the parent molecule, P.			Enthalpy of formation of I, ΔH_1 kJ/mol,	Energy required to break the bonds of the parent molecule, for the formation of the intermediate, kJ	Heat of reaction of I + P, ΔH_2 kJ/mol
	P	I	Other products			
1				350	+350	-380
2				10	+1440	-30
3				10	+1440	-540
4				120	+1875	-100
5				-230	+1875	+410
6				-90	+2640	-110
7				-30	+2640	-540
8				+610	+2640	+880

The exothermicity of the formation of the intermediate and the energy required to break the bonds, in the formation of the intermediate, are shown. The heat of reaction when the intermediate reacts with the parent molecule is shown in the final column. A negative ΔH indicates an exothermic change.

2-nitrobenzoyl chloride. The calculated heat of formation of the monomeric intermediate I, ΔH_1, for each one of the reactions of the second column, is shown in the third column. For its calculation the method shown by Craven [12] to estimate the exothermicity of a chemical reaction has been used.

The sum of the energy of all the bonds in the starting molecule was subtracted from the sum of the bond energies of the products. Average bond energies (shown in Table 4) were obtained from the literature [13]. The results of these calculations are shown in the last column of Table 3, where

the IUPAC system has been used, i.e. a negative ΔH indicates an exothermic reaction. Each of the monomer intermediates shown were suggested as possible intermediates by the results of the product analysis in our previous work [1]. These include nitrobenzyl-3-ketone, nitrobenzene, nitrosobenzene and chloronitrobenzenes. Table 3 shows that the formation of some monomeric intermediates is endothermic whilst some are exothermic. The heat of reaction, ΔH_2 when the intermediate reacts with the parent molecule, P, shown in the last column, do not always have the same thermal effect.

Table 4
Approximate bond energies of all bonds contained in the 2-nitrobenzoyl chloride molecule and molar atomisation energies of the product gases

Bond	Approximate bond energies (kJ/mol)
C_b—C_b	515
C_b—H	410
C_b—C	360
C—NO_2	1200
C—N	310
N—O	270
N=O	600
C=O	730
C—Cl	350

Possible gaseous products of decomposition	Approximate molar atomisation energies (kJ/mol)
HCl	430
CO	1080
CO_2	1610
NO	630
NO_2	950

More specifically, the formation of nitrobenzyl-3-ketone, the nitrobenzene ion, nitrosobenzene, chlorinitrosobenzene and the formation of benzyne are endothermic. In all cases, except for the benzyne intermediate, the subsequent reaction of the monomer with the initial molecule is exothermic. The enthalpy change when bonds are broken is endothermic. The energy required to break only the necessary number of bonds of the parent molecule, which will enable formation of the intermediate are shown in the fourth column of Table 3. Energy of bonds involved during recombination of parent molecule fragments for the formation of the intermediate have not been included in the calculation of the tabulated numbers of this column. Regardless of whether new bonds are formed that then make the formation of the intermediate an exothermic process energy is required to initially break those bonds. The results of these calculations show that the dichloro and trichlorobenzene monomers and the benzyne monomer require the highest energy at 2640 kJ/mol. For the nitrosobenzene monomers, 1875 kJ/mol is required to break the bonds and the monomeric intermediates needing the least energy are the nitrobenzylketone, chloronitrobenzene and nitroben-

zene monomers. At higher decomposition temperatures, the formation of dichloro and trichlorobenzene, benzyne and nitrosobenzene intermediates are more prominent. The subsequent heat of reaction, ΔH_2, when each of these intermediates reacts with the initial molecule is -540, -110, $+880$ and $+410$ kJ/mol, respectively. At lower temperatures, the formation of monomers requiring the least energy to break bonds predominates. As mentioned above these include nitrobenzylketone, chloronitrobenzene and nitrobenzene monomers that upon reaction with 2-nitrobenzoyl chloride exhibit a heat of reaction of -380, -30 and -540 kJ/mol, respectively. These findings show that at higher temperatures, the formation of intermediates that then undergo both exothermic and endothermic condensation reactions prevail. More specifically, the reaction of benzyne and nitrosobenzene with 2-nitrobenzoyl chloride have a heat of reaction of $+880$ and $+410$ kJ/mol, respectively. The dominant reactions at lower temperatures all undergo exothermic polymerisation reactions. These factors explain why the heat of decomposition is reduced as the decomposition temperature increases. The reduced volume of gas when the decomposition was carried out at 162 °C could possibly be attributed to the polymerisation of the chloronitrosobenzene monomer that is endothermic in nature and results in the formation of only one mole of gas (CO_2) as opposed to two.

As the decomposition temperature increases, the size of the first exotherm also increases. The formation of the dichloro and trichlorobenzene and chloronitrosobenzene intermediates require the highest energy to break the bonds and are the most exothermic intermediate formation steps suggesting that these reactions become more predominant as the decomposition temperature is increased.

Table 5 shows the results of all elemental analyses carried out on the decomposition residues. An "empirical formula" has been calculated to enable comparisons to be made to the composition of the original molecule with respect to the number of carbon, hydrogen, nitrogen, chlorine and oxygen atoms in a molecule having the same number of carbon atoms. Where the sample was held at 150 °C, the average Cl content was reduced from 12 to 7 atoms in a molecule containing 84 carbons. The same reduction is shown for a molecule that has undergone decomposition at 162 °C. In the 150 and 162 °C

Table 5
Results of the elemental analysis and oxygen flash combustion followed by titration with mercuric nitrate for samples decomposed at 150 and 162 °C, following a 2 °C/min heat up rate, 7.5 °C/min heat up rate and in the presence of metals

Details (reactor steady-state temperature (°C) heating rate applied from 40 °C to bring sample to required temperature (°C/min)), mode of operation, experiment number	Element (%)					Empirical formula
	C	H	N	Cl	O	
150 °C, 2 °C/min, HF, **1**	50.15	2.1	7.55	12.7	27.5	$C_{84}H_{42}N_{11}O_{35}Cl_7$
162 °C, 2 °C/min, IP, **4**	50.55	2.25	8.3	12.95	25.95	$C_{84}H_{45}N_{12}O_{32}Cl_7$
162 °C, 7.5 °C/min, IP, **10**	51.3	2.45	8.35	11.5	26.4	$C_{84}H_{45}N_{12}O_{32}Cl_6$
Continual heating, no steady-state temperature (hotplate)	59.7	2.8	10.2	12.4	14.87	$C_{84}H_{48}N_{12}O_{15}Cl_6$
157 °C, 2 °C/min, iron powder present, IP, **7**	50.75	2.35	8.1	12.1	27.5	$C_{84}H_{47}N_{11}O_{34}Cl_7$
Initial molecule, 2-nitrobenzoyl chloride	45.4	2.2	7.6	18.9	26	$C_{84}H_{48}N_{12}O_{36}Cl_{12}$

The results of the analysis following the decomposition of a sample that was continuously heated is also included and the % composition of the original sample. HF, heat flow mode; IP, isoperibolic mode.

Table 6
Summary of results obtained when samples were heated at 2, 3 and 7.5 °C/min from 40 to 162 °C

	Experiment		
	4	5	6
Experimental temperature (°C)	162	162	162
Sample mass (g)	14.023	15.158	14.710
Steady-state reactor temperature (°C)	161.4	162.1	160.9
Sample heating rate (°C/min) (from 40 °C to desired temperature in reactor)	2	3	7.5
Total heat output (kJ)	7.5	11	17
Heat of decomposition (kJ/mol)	90	115	215
Volume of gas produced (ml)	400	450	520
Temperature at start of gas flow (°C)	150	151	146
Jacket temperature (°C)	161.1	160.9	161
Maximum reactor temperature (HF) or maximum temperature reached during first stage in the decomposition (IP mode)	164.6	165	164.5
Maximum temperature achieved in second stage of decomposition (°C) (IP mode only)	164.7	164.8	250
Maximum temperature difference between jacket and reactor (°C)	3.6	3.9	89
Time taken for decomposition to proceed, min	89	99	70
Number of stages of decomposition	Two	Two	Two

All experiments were carried out in isoperibolic mode with the sample fully agitated throughout.

run, the oxygen content of the molecule is reduced from 36 to 35 and 32, respectively. These results show that the loss of oxygen from the molecule is slightly increased with increasing temperatures. The argument set out above to justify the reduced heat of decomposition with increasing temperature is supported by the lower oxygen content of the sample that underwent decomposition at a higher temperature.

4.3. Effects of initial heating rate on sample decomposition

Table 6 shows a summary of the results of the sample decomposition when the sample heat up rate was increased. Experiment 4 from the previous round of experiments is included as the sample was heated at a rate of 2 °C/min to 162 °C. In experiment 5, the heating rate was increased to 3 and 7.5 °C/min in experiment 6. As the heating rate increases the heat of decomposition is also shown to increase, where the sample was initially heated at a rate of 2.3 and 7.5 °C/min, the total heat output was 7.5, 11 and 17 kJ, respectively. These values correspond to a heat of decomposition of 90 kJ/mol (2 °C/min), 115 kJ/mol (3 °C/min) and 215 kJ/mol (7.5 °C/min).

Fig. 4 shows the power output and temperature profiles for experiments 4–6, where different heating rates are employed. Where the sample is heated at 2 and 3 °C/min, the temperature history and power output follow very similar profiles. In the embedded figure, the scale of the representation of the power generation profile for these measurements to be seen more clearly. The shape of the profiles is exactly the same
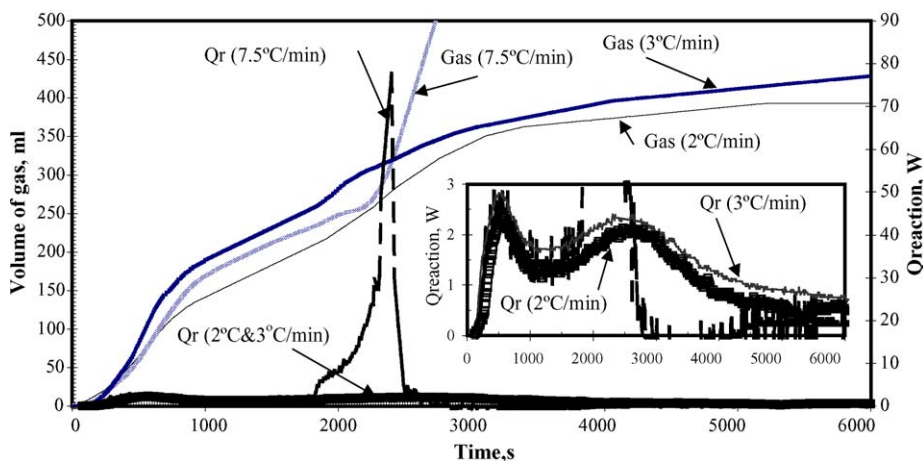

Fig. 4. Gas production and power output profiles for the decomposition taking place following various initial heating rates. In all runs, the sample was heated from 40 to 162 °C at 2, 3 and 7.5 °C/min. Q_r indicates the power generation. Gas production in millilitres.

for the first stage of decomposition (first peak). However, the power output profiles of the second stage of decomposition (second peak) depend on the heating rate of the sample. The power output and temperature profiles following the maximum heat up rate of 7.5 °C show that the second exothermic peak is much more pronounced than in the 2 and 3 °C heat up rate experiments. A heat up rate of 7.5 °C/min initiates an exotherm of a much greater magnitude in the second stage of the decomposition. These findings show that a small increase in the heating rate from 2 to 3 °C/min has a small influence on the temperature progression of the reaction and its power output. A significant initial heating rate does not alter the progression of the decomposition in its first stage but greatly affects the magnitude of the second exotherm.

The maximum temperature attained by the sample during the second stage of the decomposition is 250 °C in contrast to maximum temperatures of 164.7 and 165 °C attained in the 2 and 3 °C/min heat up measurements, respectively. In experiments 4 and 5 (2 and 3 °C/min heat up rates), the two maximum temperatures achieved in each exotherm differ only slightly: 0.1 °C in the experiment 4 and by 0.2 °C in experiment 5.

The pronounced exothermicity induced at increased heating rates can be attributed to the exothermic decomposition paths predominating under these conditions. As the heating rate was increased to 7.5 °C/min, the heat of decomposition was increased by 100 kJ/mol. This suggests that the formation of intermediates 6 and 7 and their subsequent polymerisation reactions predominate following an initially faster heat up rate. Faster heat up rates can also reduce the amount of heat lost to the surroundings during the heat up period, thus increasing the heat supplied to the sample. Perhaps, during a faster heat up period, less time is available for immeasurable thermal events to take place that can then be accounted for at a later stage in the measurement. The results of the elemental analysis provide evidence in support of this theory and show a greater reduction in the oxygen content of the molecule following a 7.5 °C/min heat up rate in comparison with the 150 °C run. In our previous work [1], a sample contained in a small vial was heated continuously from room temperature to 250 °C, until decomposition was complete. The results of the elemental analysis carried out on the solid residue showed that the oxygen content of the molecule was drastically reduced in addition to the reduction in chlorine seen in all measurements.

The cumulative gas evolution profiles for the various heating rates investigated are also shown in Fig. 4. The gas evolution profiles for the decomposition of the samples following a 2 and 3 °C/min heat up rate are very similar in shape with the highest heat up rate resulting in the greatest evolution of gas. During the first stage of the decomposition, the gas evolution profile for the sample that had been heated at a rate of 7.5 °C/min from room temperature lies between that of the 2 and 3 °C/min gas evolution profiles.

As the second stage of the decomposition is initiated, the gas evolution rate increases rapidly before terminating. The rate of gas evolution always corresponds to the slope of the power output profile. In the initial stages of the first exotherm following the 3 °C/min heat up period, the rate of gas evolution (and slope of the power output profile) is steeper than that of the 2 °C/min run before the gradient of the power output profiles and gas evolution become equal.

Volume of gas production also appears to increase with increasing heat up rate. Following a 2 °C/min heat up rate, 400 ml gas had been produced. During decomposition of the sample heated at 3 °C/min, the total volume of gas produced was increased to 450 and 520 ml when a 7.5 °C/min heat up rate was employed. In all of the experiments carried out to investigate the effects of the initial heat up rate, 400–520 ml gas was produced. Each experiment was carried out at 162 °C. In experiments 1–3, where the sample was decomposed at 150, 153 and 157 °C, the volume of gas produced ranged from 650 to 720 ml. These findings suggest that at 162 °C, reactions that evolve less gas prevail. For example, reaction 6 results in the formation of only one mole of gas in contrast to the majority of the others that generate two moles of gas per mole of 2-nitrobenzoyl chloride. Another possible explanation is the consumption of HCl by the polymerisations taking place, however, this difference could be partially or entirely due to the overhead gas expansion which does not presumably cool sufficiently at faster heating rates.

4.4. Effect of the presence of metals and calibrations performed before decomposition

Table 7 shows the results of three experiments carried out at 157 °C and one at 153 °C. Experiment 3 was carried out using 14.5 g sample and the calorimeter was operating in heat flow mode. Experiment 7 was carried out to determine the effects of iron powder on the decomposition. In experiment 8, 17.1 g sample was decomposed following calibrations at 60, 80 and 100 °C. Lastly, in experiment 9, 18.5 g sample was decomposed in the presence of silver and following calibrations at 40, 80, 110 and 130 °C. Two sets of calibrations had been carried out at 80 and 110 °C.

In both experiments 7 (isothermal) and 8 (metals), the decomposition was seen to proceed by in two stages. The samples that had undergone calibrations were cooled to 40 °C and heated at a rate of 2 °C/min to 157 °C (same as experiments 3 and 7). This step was carried out to ensure that the samples were subjected to the same temperature treatment, as samples that did not undergo calibrations, during the heat up period. Although following calibrations prior to decomposition in both experiments 8 and 9, the samples were cooled to 40 °C and then reheated at the same rate as in experiments 3 and 7 (two-stage decomposition), the decomposition took place in one stage only. These findings indicate that some chemical changes occur, where calibrations take place earlier in the measurement that in turn affect the mechanisms by which the decomposition proceeds.

Table 7
Summary of results obtained when the decomposition was carried out isothermally, in the presence of iron powder and following calibrations at 60, 80 and 100 °C

	Experiment			
	3	7	8	9
Experimental temperature (°C)	157	157	157	153
Details	Isothermal	With iron powder	Calibrations before decomposition at 60, 80 and 100 °C	Calibrations at 40, 80, 110 and 130 °C, silver present
Sample mass (g)	14.495	14.765	17.123	18.543
Steady-state reactor temperature (°C)	157.1	156.9	156.6	153.3
Mode of operation	HF	IP	IP	IP
Total heat output (kJ)	15.4	12.6	15.3	10.9
Heat of decomposition (kJ/mol)	185	160	170	110
Volume of gas produced (ml)	760	330	–	–
Temperature at start of gas flow (°C)	147	140	147	–
Minimum jacket temperature (°C) (HF) or jacket temperature (IP)	153.6	156.3	156.3	154.7
Maximum T_R (HF) or max T_R reached during first stage of decomposition (IP)	156.8	161.8	158.7	159.4
Maximum temperature in second stage of decomposition (°C) (IP mode only)	–	158.7	–	–
Maximum ΔT between jacket and reactor (°C)	3.2	5.5	2.4	4.7
Time of decomposition (min)	287	179	216	148
Number of stages of decomposition	Two	Two	One	One

Samples were heated from 40 °C to the desired temperature at a rate of 2 °C/min. They were continuously agitated throughout.

The heat of decomposition calculated for the measurements with and without calibrations is −165 and −185 kJ/mol, respectively. In the presence of silver and following numerous calibrations, the total heat output for the 18.5 g sample was reduced to −10.9 kJ corresponding the a heat of decomposition of −110 kJ/mol. The overall exothermicity of the process is, therefore, reduced by calibrations carried out before decomposition. This finding could be attributed to the occurrence of thermal events at temperatures below which decomposition takes place to a measurable extent that, during calibrations have more time to take place. These may promote endothermic reactions during sample decomposition that in turn reduce the overall exothermic-

ity. Because more calibrations were carried out prior to the decomposition of the 18.5 g sample, these endothermic events could have been more prominent thereby further reducing the measured heat of decomposition. Where the heat up phase took place in stages (isothermal, 150 °C), a one-stage decomposition was observed. These changes occur during heat up, regardless of whether the sample is heated in stages, as proven by the results obtained, where the sample was heated at a rate of 7.5 °C/min. The samples from experiments 8 and 9 were cooled back to 40 °C after calibrations and then heated at 2 °C/min to 157 and 153 °C for decomposition. This step was carried out to ensure that the heat up phase of the measurement mirrored that of the other experiments. In both cases,
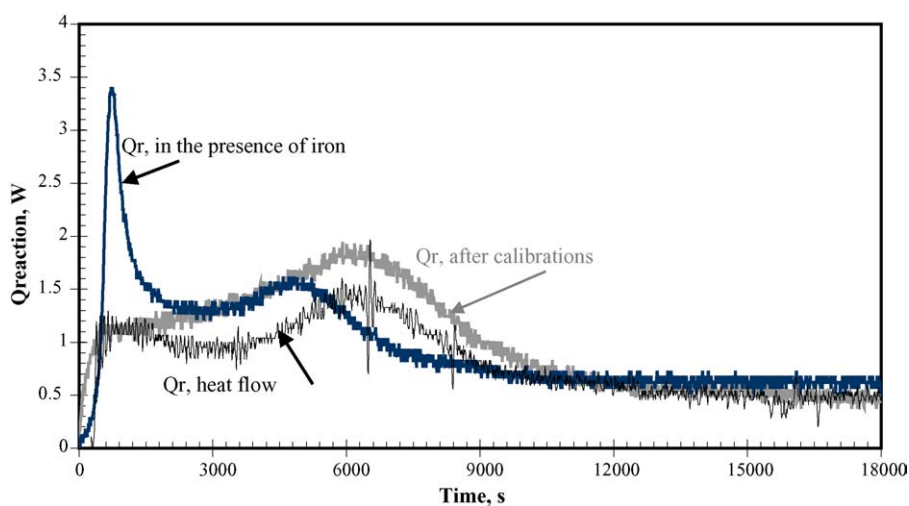

Fig. 5. Power output and temperature profiles for the decomposition of 2-nitrobenzoyl chloride in the presence of iron powder, following calibrations and in heat flow mode. All experiments performed at 157 °C.
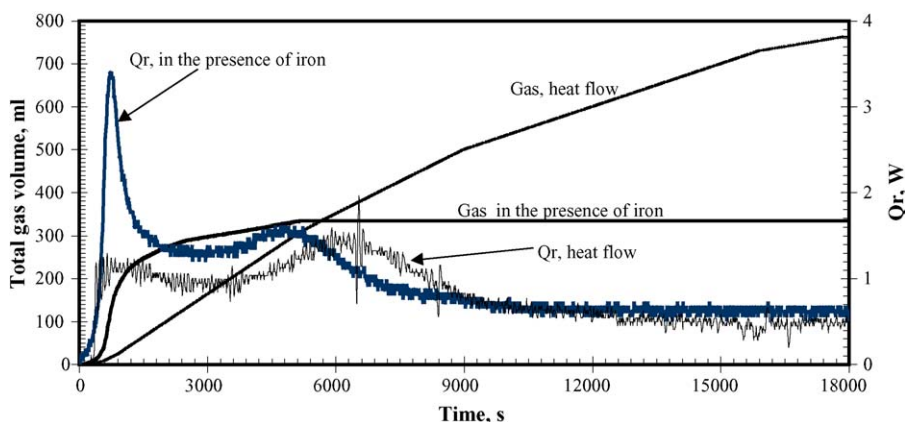
Fig. 6. Power output and cumulative gas production for the decomposition of 2-nitrobenzoyl chloride in the presence of iron powder and in heat flow mode. Both experiments were performed at 157 °C.

the decomposition took place in one stage indicating, again, that the sample had undergone some chemical changes during calibrations that in return influenced the decomposition.

In both experiments 3 and 8, the production of gas started at 147 °C. The sample that had been subjected to calibrations prior to decomposition decomposed in 216 min taking less time than the untreated sample, which took 287 min to decompose. Where more calibrations had been carried out and at higher temperatures, the duration of decomposition was further reduced to 148 min. The reduced decomposition time is probably due to some of the decomposition having taken place during calibrations.

Figs. 5 and 6 show gas evolution and power output profiles for three experiments at 157 °C. Where 0.002 g iron powder was present, the heat of decomposition was reduced from 185 to 160 kJ/mol. Fig. 5 shows a two-stage decomposition for the reaction taking place in the presence of iron. The first exotherm is more pronounced in the presence of metals than in the isothermal measurement. Gas evolution started at an earlier temperature of 140 °C when iron was present (Fig. 6). On addition of the iron to the sample at room temperature, a colour change from tan to dark brown took place. This colour change was apparent in all measurements, however, did not occur until a later stage in the heat up period suggesting that the colour change can be attributed to the initiation of some chemical change by the presence of iron. Metals are known to catalyse Friedel Crafts reactions that have been verified to take place during decomposition by our previous work [1]. The increased pronunciation of the first exothermic peak is probably due to the catalysis of more exothermic reactions in the presence of iron. Overall, the heat of decomposition in the presence of iron is reduced. The more pronounced peak in the first stage of the exotherm can probably be ascribed to reactions similar to that of Scheme 6 shown in Table 3, where the formation of the intermediate is exothermic and the subsequent polymerisation is endothermic.

The advent of gas evolution at the earlier temperature of 140 °C and the increased rate of heat production (hence, rate of reaction) can be attributed to the catalysis of the reactions

by iron. Fig. 6 shows that the initial rate of gas evolution is much greater in the presence of iron. In the presence of iron, the total volume of gas produced is reduced by more than 50%. Once more, this reduction can be attributed to the prevalence of reactions like those taking place in Scheme 6. The reduction in the heat of decomposition in the presence of silver to 110 kJ/mol, where the sample had undergone multiple calibrations can probably be partly attributed to the presence of silver in addition to the effects of calibrations.

5. Conclusions

A calorimetric study has been carried out on the decomposition of *o*-nitrobenzoyl chloride using both heat flow and isoperibolic measurements to determine the apparent onset temperature and heat of decomposition. The effects of decomposition temperature, the heating profile applied to bring the sample to decomposition temperature and the presence of silver and iron have been investigated. As the temperature of decomposition was increased from 150 to 162 °C, the heat of decomposition was reduced from −215 to −90 kJ/mol. As the heat up rate applied in bringing the sample to the decomposition temperature increased, the heat of decomposition also increased. An increase in the heat up rate from 2 to 7.5 °C/min resulted in an increase in the heat of decomposition from −90 to −215 kJ/mol. The presence of iron and silver was observed to lower the heat of decomposition from −185 to −160 and −110 kJ/mol, respectively. The much lower value obtained for decomposition in the presence of silver was also due to numerous calibrations having been carried out prior to sample decomposition. In two experiments, calibrations were shown to reduce the heat of decomposition. In the sample that had undergone more calibrations and at the higher temperatures, the heat of decomposition was reduced to the greatest extent. Under most conditions investigated, the temperature at which gas flow was initiated was 147–150 °C. The presence of iron reduced this temperature to 140 °C. Decomposition was observed to take place over

two stages, where the sample was heated directly from 40 °C at the required heat up rate. Where the sample was heated in stages and where calibrations had been carried out preceding decomposition, the decomposition took place in one stage alone. These findings are most likely to be due to the occurrence of thermal events during heat up that consume some of the heat of decomposition. The heat of reaction for the formation of probable intermediates and their subsequent polymerisation reactions has been calculated. The results of these calculations showed various degrees of exothermicity in addition to endothermic polymerisation reactions taking place. The high condition dependency of the decomposition of 2-nitrobenzoyl chloride can, therefore, be attributed to the predominance of different reaction paths under different conditions that exhibit conflicting thermal effects on the decomposition.

Acknowledgements

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