

THE THERMAL STABILITY OF ALKYL HYPOCHLORITES

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Environmental and economic constraints on the chemical industry are increasing. Process intensification means that waste streams are often either recycled or alternative uses found for them. Due to its oxidative properties industrial strength bleach, itself often arising as an effluent from chlorine scrubber systems, is commonly used in effluent treatment processes to remove malodorous materials such as sulphur compounds. In terms of process safety this introduces potential hazards due to the incomplete consideration of possible undesirable reactions. Of particular interest are the reactions that occur on mixing sodium hypochlorite (bleach) with alcoholic reaction masses (either organic or aqueous) as this can lead to the generation of thermally unstable, highly explosive alkyl hypochlorites, (methyl hypochlorite in particular being classified as a high explosive having a similar explosive potential to TNT). This paper provides details of an investigation into the thermal stability of the lower homologues of this series using a variety of experimental techniques to determine the relationship between thermal stability and time during decomposition.

INTRODUCTION

Within the process industries a large amount of resource is utilised to ensure that chemical processes are operated safely. The primary focus tends to be on the desired reaction as it is often perceived that this is where the major hazards will occur, best practice guidelines^(1,2) are usually targeted towards this area. Whilst this is undoubtedly the case in many situations the operations carried out both up and down stream of the main reactor also need to be considered in some detail. Effluent treatment can be a particular issue as focus can be lost due to the perception that 'we are only treating a waste so it won't be a problem'. A typical example would be the oxidation of a sulphide to a sulphoxide using hydrogen peroxide in methanol. After extraction and separation the chemist would be left with a potentially malodorous solvent mass which would need to be disposed of. Clearly it would be undesirable to dispose of this without treatment and the obvious way to get rid of the smell would be to treat with sodium hypochlorite, whilst this is likely to be effective there is an inherent risk associated with this as the alcohol left in the effluent could react with the bleach to form methyl hypochlorite. This paper focuses upon one particular class of materials, alkyl hypochlorites, which have been identified as being present in waste streams after treatment has been carried out and have also been cited as the reason for explosions⁽³⁾.

PROPERTIES OF ALKYL HYPOCHLORITES

The first reported work on alkyl hypochlorites – specifically methyl and ethyl hypochlorite – was carried out by Sandemeyer^(4,5) in the 1880's. He showed that the materials were relatively insoluble in water and had a tendency to separate out as a yellow oil. This oil decomposed on heating or exposure to light. In the 1920's Chattaway et al.⁽⁶⁾ carried out work on other hypochlorites such as propyl and butyl. They determined that in relative terms the alkyl hypochlorites became progressively more stable as one moved through

the homologous series and/or increased the branching in the molecule, in addition it was found that they are unstable at high concentrations and under certain conditions some can exhibit explosive properties. They also tend to have limited water solubility leading to the possibility of a formation as a separate phase on cold surfaces.

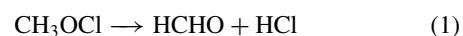
Specific testing of methyl hypochlorite for explosive properties⁽⁷⁾ showed that it was heat, light and shock sensitive with a heat of decomposition of ca. 3000 J/g. Trautzl Lead Block testing showed that the neat material has properties similar to TNT and acetone hydroperoxide.

Bretherick's Handbook of Reactive Chemical Hazards cites a number of incidents which have been attributed to the presence of alkyl hypochlorites generated during waste treatment operations. All lead to explosions, but thankfully no reported fatalities, however it should be noted that there is only circumstantial evidence relating to the presence of alkyl hypochlorites.

MECHANISM FOR DECOMPOSITION

A literature review highlights some uncertainty over the actual chemistry which occurs during decomposition. For methyl hypochlorite the following have been postulated and similar mechanisms are proposed for other alcohols.

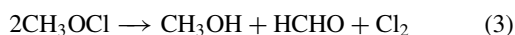
Work by Chattaway et al. indicated that the primary products were the corresponding aldehydes or ketones along with HCl. This can be represented by the following equation



There have also been suggestions that during the synthesis of the alkyl hypochlorites, esters are formed as follows⁽⁸⁾:



Subsequent work by Durand et al.⁽⁹⁾ suggested that chlorine was also produced.



Unpublished work carried out in the 1970s within a legacy company of Syngenta on the properties of methyl hypochlorite postulated the following



As part of the work carried out on the postulated reaction 4, a value for the enthalpy of formation was calculated as -10 ± 10 kJ/mol. More recent data from Bozzelli et al.⁽¹⁰⁾ suggests that the enthalpy of formation of methyl hypochlorite is significantly higher at around -64.5 ± 6.2 kJmol⁻¹. This does seem to be a more acceptable value when compared to that of hypochlorous acid itself which is quoted as -74.5 kJmol⁻¹ (see Table 1).⁽¹¹⁾

Experimental investigations have shown that the heat of decomposition of neat methyl hypochlorite is around -3000 J/g. This suggests that route 2, i.e., formation of methyl formate and two mol of HCl gas is most likely. If undiluted, then in theory, the decomposition of methyl hypochlorite could generate an adiabatic temperature rise of >1000 K. The change in volume (due to methyl formate vapour and HCl gas generation), would be up to 1150 times i.e., significant over-pressurisation could occur.

Regardless of the pathway if the undiluted material were to decompose we would have a problem.

The thermochemical calculations can only be taken as indicative of the likely mechanism and further experimental evaluation is required.

EXPERIMENTAL INVESTIGATION

The work by Sandmeyer and Chattaway used similar synthetic routes with chlorine gas being bubbled through a solution of sodium hydroxide in alcohol, conditions which would be unlikely in a waste treatment scenario. A more realistic approach (see Appendix 1) in which alcohols were simply mixed with sodium hypochlorite was therefore adopted.

The original intention had been to examine the thermal stability of a series of alcohols with an increasing chain length and degree of branching then carry out kinetic modelling (using model free kinetics) in order to obtain a means of predicting the stability of the materials. Initial raw DSC data files used to screen ethyl hypochlorite

and 2-butyl hypochlorite were supplied by J Kay at HSL, Buxton and this data was analysed by Syngenta and considered alongside internally generated data. The analysis of that data is considered below.

Initial attempts were made to produce methyl hypochlorite however it was not possible to isolate this in sufficient quantity using the synthetic route used to allow testing, the investigation was therefore extended to include ethanol, butanol and 2-butanol.

DSC testing on ethyl hypochlorite (Figure 1) gave a very distinct non-symmetrical peak which is indicative of autocatalytic behaviour. With an autocatalytic system using a standard Model-Free Kinetics (MFK) analysis we would be unlikely to determine a satisfactory model, and attempts to produce a consistent data set were unsuccessful. The total heat output based upon actual ethyl hypochlorite content was in excess of 2100 J/g.

We therefore turned our attention to other alcohols, i.e., n-butanol and 2-butanol.

Literature reports suggest that chain branching results in more stable hypochlorites. The initial test at 4 K/min on the 2-butyl hypochlorite (Figure 2) indicates that the decomposition is not simple as there is evidence of a shoulder on the main decomposition peak. Again attempts to produce a consistent data set for analysis using model free kinetics proved unsuccessful with significant differences in peak shape height and temperature being noted.

The investigation into n-butyl hypochlorite was slightly more promising and scans were carried out at 2 K, 5 K and 10 K/min (Figures 3–5). There is still a degree of variability in the peak profiles with the 5 K ramp (Figure 4) showing the presence of a distinct shoulder prior to the main peak, the heat outputs and the peak positions are however reasonably consistent with an overall heat output in the range of 1700–1800 J/g. With a fairly consistent data set the application of an MFK model indicated that there would be little or no decomposition occurring below 30°C, however the data did not produce a very convergent model which suggests that this may not be an accurate prediction of the real situation. The isothermal Carius tube work described later confirms that this MFK model may not be an accurate simulation of the actual decomposition.

In parallel to the work using DSC an investigation using Carius tubes, focussed on butyl hypochlorite, was also carried out. The basic principle of this technique is to heat the sample up in a glass Carius tube at a constant

Table 1. Calculated values for reaction enthalpy and decomposition energy

Reaction	Reaction enthalpy (calculated ΔH_f MeOCl) kJmol ⁻¹	Decomposition energy (J/g)	Reaction enthalpy (Bozzelli ΔH_f MeOCl) kJmol ⁻¹	Decomposition energy (J/g)
1	-198	-2980	-138	-2075
2	-530	-7970	-205	-3080
3	-157	-2510	-37	-1610
4	-192	-2890	-132	-1985

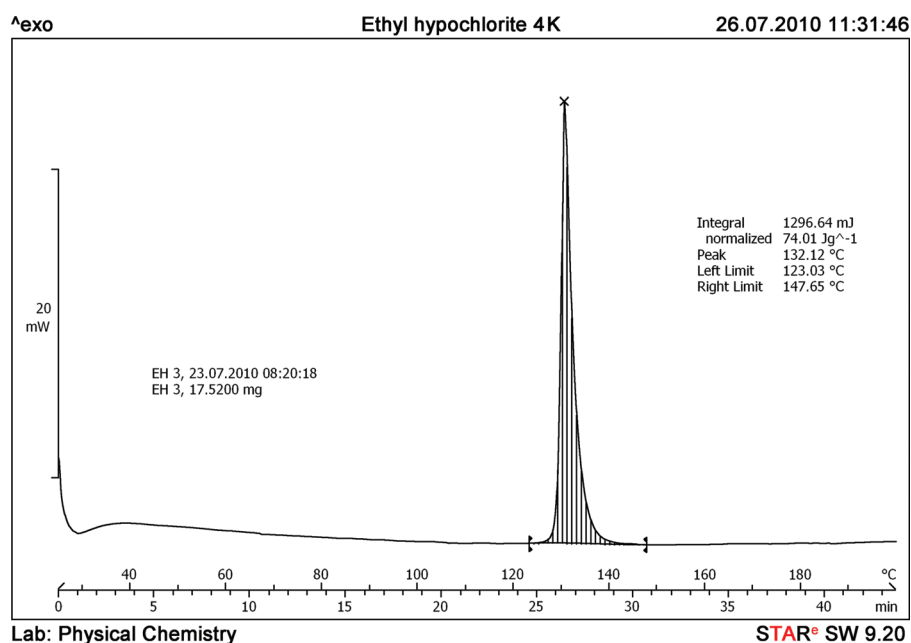


Figure 1.

ramp rate (2 K/min gives the optimum balance between resolution and sensitivity) whilst monitoring the sample temperature and pressure. In terms of sensitivity, detection of exotherms occurs when heat outputs are in the range 3–10 W/kg which is slightly better than typical DSC measurements (10–20 W/kg).

Our standard approach is to carry out duplicate testing both with and without typical materials of construction

(mild steel, stainless steel and cast iron). In the absence of metals decomposition was apparent from around 55°C with a peak at around 85°C. When metals were present exothermicity was apparent from ca 43°C with a peak at 77°C, there was also evidence of further mild exothermic activity from around 125°C (see Figure 6).

The shape of the exotherms (Figure 7) is also somewhat different. In the presence of metals the exotherm is

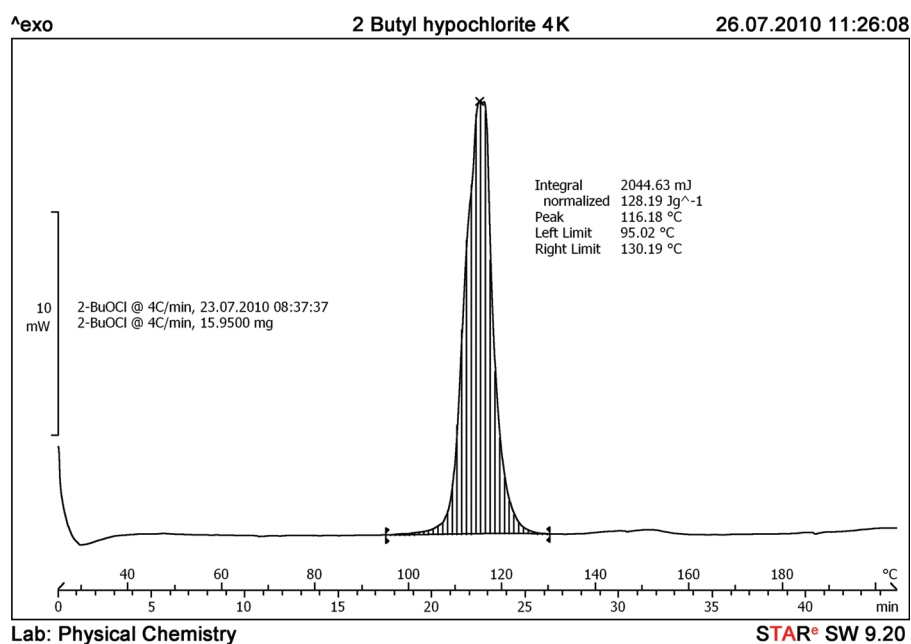


Figure 2.

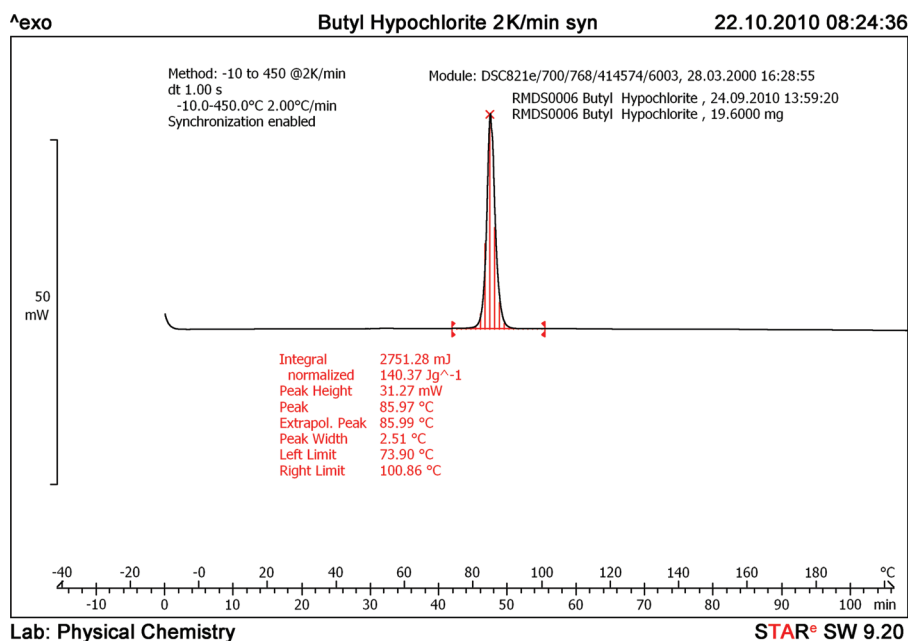


Figure 3.

more gradual whereas in the absence of metals the start of the exotherm is quite sharp suggesting that some form of catalytic effects are being introduced as a result of the presence of metals. Also the exotherms are somewhat different to those seen in the DSC as they are apparent from lower temperatures and are, on a purely qualitative basis, less energetic.

Both tests indicate that gas evolution occurs from around 60°C. If it is assumed that the reaction is the same in each case and that the gas formed in the decomposition is HCl then the residual pressure at the end of each experiment will provide an indication of the total volume of gas evolved in each case. One factor which we cannot quantitatively account for is the quantity of gas dissolved in each

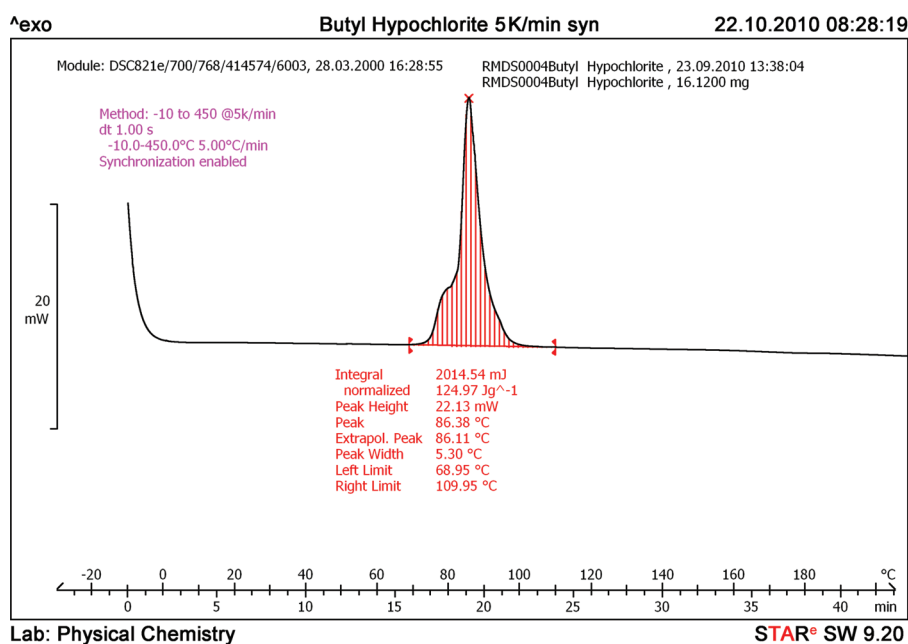


Figure 4.

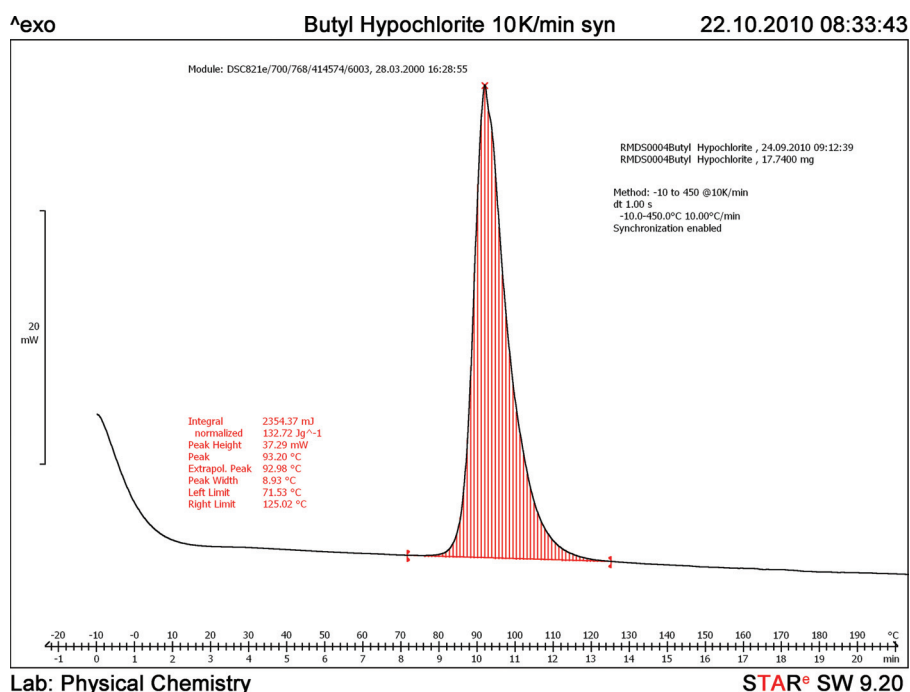


Figure 5.

reaction mass at the end of the test. However as the same quantity of material was used in each test we can safely assume that the solubility levels will be comparable, using this assumption it can be shown that in the presence of

metals approximately 50% more gas is formed, i.e., a different mechanism is occurring in the presence of metals.

If we take a simple rule of thumb based around the premise that the rate of reaction approximately doubles

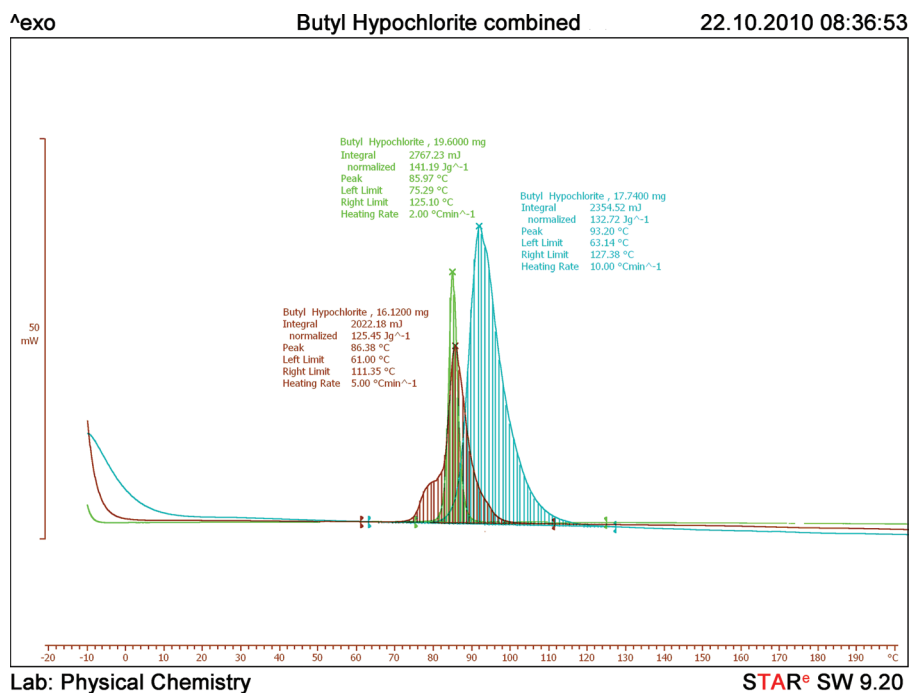


Figure 6.

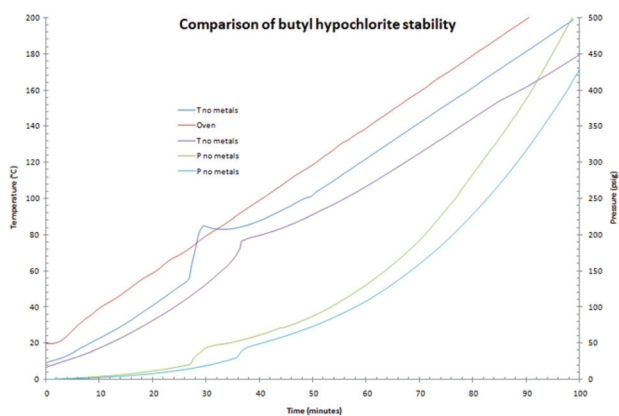


Figure 7.

for every 10 K rise in temperature then we can assume that on increasing scale as the heat losses will decrease we could expect the decomposition to be apparent from a lower temperature. Whilst it is difficult to specify the scale in a waste treatment scenario, comparison can still be made between the DSC results and the Carius tube data. In the butyl hypochlorite DSCs the temperature at which exothermicity was detected (left limit on trace) was ramp rate dependant but was typically in the range 80–100°C, the sample size was around 20 mg, therefore if this were scaled up one could sensibly expect that the exotherm could be detected on a 10 g scale in the region of 50–70°C. Whilst this is a very much an approximation it does give an indication that the results from the DSC and those from the Carius tube are comparable.

Consideration of the DSC data indicates that we are unable to get good reproducibility on repeat tests when using either fresh or stored material, whilst the reason for this is not immediately clear the influence of the material of construction could be an important factor. The Carius tube results clearly show that the presence of metals has an impact upon the thermal stability profile, as there is a distinct difference in the profiles obtained in the glass tubes if metals are present.

In a waste treatment scenario it is highly unlikely that we would be dealing with a 'clean' system as metals and other contaminants are likely to be present, it was therefore decided that further investigations would be carried out in the presence of metals.

As the thermal event is accompanied by the generation of gas or volatiles it is possible to use the pressure data to determine kinetic parameters for a decomposition reaction (Figures 8 & 9).

Testing was carried out at 19°C, 25°C and 29°C. If we first examine the temperature data it can clearly be seen that the decomposition is more complex than the dynamic testing would suggest and from the initial dynamic screen it would not be possible to predict what is likely to be apparent under isothermal conditions. At 19°C and 25°C there are clearly two distinct events apparent, but at 29°C there is also

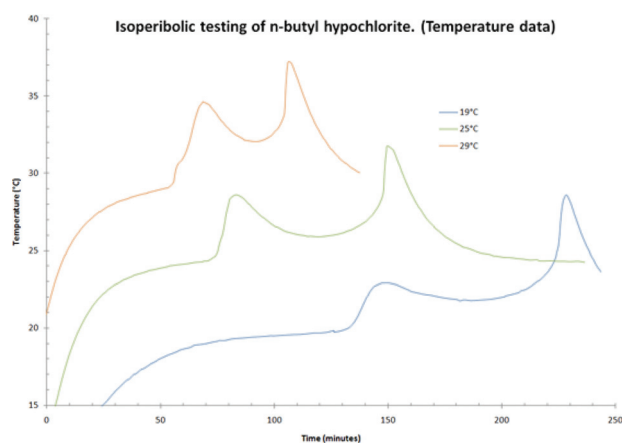


Figure 8.

evidence that a third event is occurring. This is again indicative of an autocatalytic decomposition process.

Due to the nature of the test the pressure measurements tend to give a more sensitive indication of when an event is starting to occur. If we take the start of acceleration of the rate of pressure rise as an indicator of the decomposition then analysis shows that at typical ambient temperatures (18–25°C) the induction time prior to decomposition being apparent would be of the order of 1–2 hours (see Table 2).

TGA/STA/EVOLVED GAS ANALYSIS

Freshly prepared samples of butyl hypochlorite in DCM were analysed using a Perkin Elmer STA6000 coupled to a Hiden HPR-20 Mass spectrometer. The results (Figures 10–11) show that on heating there is mass loss from below 40°C. This mass loss is accompanied by an endothermic event which may be due to the volatile nature of the solvent.

In order to determine if the endotherm was simply due to the vaporisation of the DCM solvent a blank experiment

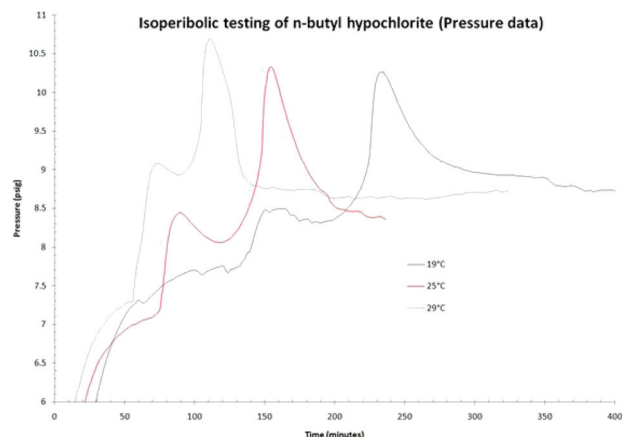


Figure 9.

Table 2. Gas evolution induction times

Temperature (°C)	Time to start of gassing (hours)	Time to peak rate (hours)
20	1.8	2.3
40	0.8	1.1
60	0.35	0.5

was carried out on a sample of the solvent which showed a different thermal profile. This suggests that the heat of decomposition of the non-DMC components is of the order of -1200 J/g, i.e., lower than expected from the DSC results if it were simply the alkyl hypochlorite decomposing in the same manner.

Analysis of the mass spec data indicates the presence of the following components, HCl, Butanal, Butyl esters, Alkyl chlorides, Chloro butanol. There is no evidence of the presence of either chlorine or carbon monoxide, which effectively discounts the postulated mechanisms 3 and 4.

DISCUSSION

The initial postulation of the decomposition of an alkyl hypochlorite resulting in the formation of HCl gas and an ester looks to be quite sound based upon the calculated values for the heats of formation. Indeed with experimentally determined heats of decomposition in the range -180 to -206 kJmol⁻¹ we have what appears to be a very plausible explanation.

However, what appears at first to be a relatively straight forward decomposition reaction is in fact quite complex. The experimental results indicate that the decomposition is test method dependant and such factors as the materials of construction, heating rate, time and light all appear to have an influence on not only the rate but also the reaction pathway.

Both the TGA and the DSC have been calibrated against the same standard (Indium) and as such all things

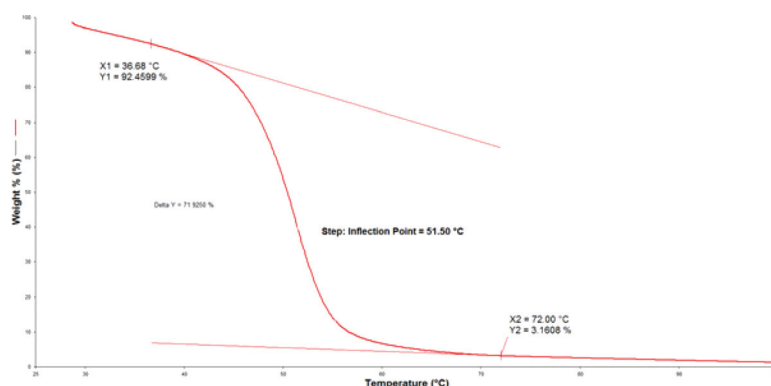
being equal similar results would be anticipated. As this did not occur it suggests that the difference in heat output is likely to be genuine, again pointing to a variety of decomposition mechanisms being possible. Literature sources indicate that the presence of HCl (and also pH) will catalyse the decomposition of alkyl hypochlorites. In the case of the DSC and Carius tubes the systems are sealed so any HCl generated will remain in the reaction mass which could enhance the decomposition. In the TGA/STA work the system is unsealed and any HCl generated would be evolved thereby reducing the potential for any catalytic effects from this source to be apparent. In addition to this the volatility of the materials could also be a factor as in an open system they could be vaporised prior to undergoing complete decompositions.

Due to the complex and apparently variable nature of the decomposition attempts to produce an accurate kinetic model for the decomposition of the alkyl hypochlorites have so far proved unsuccessful.

This leads us to the following questions:

- (1) How does the data generated relate to a large scale waste treatment plant operation?
- (2) How can the presence of alkyl hypochlorites be prevented? Or indeed do we need to prevent it?

For a synthetic route the answer is fairly straightforward in that early process development can allow the potential hazard to be designed out by the use of alternative reagents, simple changes to the engineering design or

**Figure 10.**

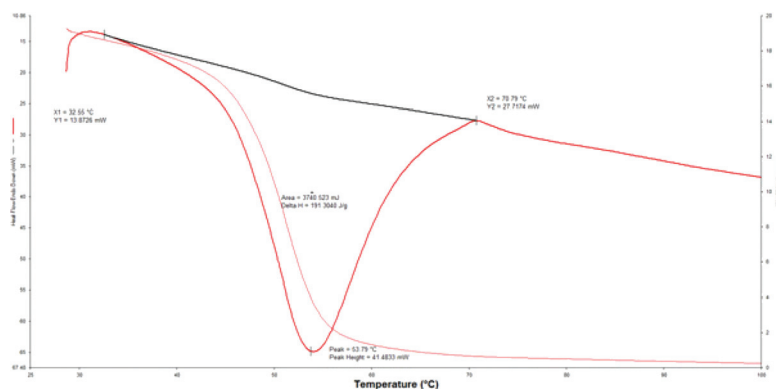


Figure 11.

the use of effective process control. For example in the scenario of cleaning up a sulphur containing aqueous methanol stream we may be able to change the process such that methanol is not used and the system is completely aqueous.

For the waste treatment situation similar criteria could be used in order to minimise the potential for formation. Whereas this approach could be feasible for an engineered in-process waste treatment process where the effluent streams have been fully characterised it may not be acceptable or even achievable when multiple streams of variable, possibly, unknown composition are being handled. In this situation we would need to look deeper into the potential scenarios in order to determine the following:

- (1) Can alkyl hypochlorites be formed?
- (2) If so under what conditions?
- (3) If they are formed would they be formed in sufficient quantity to cause a problem.

The literature search indicated that pure alkyl hypochlorites can be formed in the laboratory by the action of chlorine gas on alcohols under controlled conditions, i.e., a situation that is unlikely to occur in a waste treatment facility. Our experimental investigation has shown that the hypochlorites can be formed relatively easily by the action of sodium hypochlorite on an alcohol under laboratory conditions. By using such clean conditions we cannot prove that we would form the materials in effluent treatment but equally we cannot disprove it. Therefore we must assume a worst case situation, i.e., that formation will occur.

Initial attempts to isolate methyl hypochlorite showed that it was either extremely volatile or unstable. At ambient temperatures, on a large scale if conditions conducive to the formation of the material occurred then although it is not possible to quantify the amounts one could expect that the majority of the material would either be vaporised due to the low boiling point or decompose as it is formed. Provided that no cold spots existed in the plant then accumulation of the material would not be expected and the potential hazard

within a well designed facility would not be significant although could not be ruled out.

For n-butanol we have shown that a gas evolving thermal decomposition will occur even at room temperature. The decomposition is not however instantaneous and could cause a problem in a waste treatment situation as it means that a build-up of material could occur which in turn could result in a sudden decomposition.

CONCLUSIONS

- (1) Simply mixing an alcohol with sodium hypochlorite can result in the formation of a thermally unstable material.
- (2) The materials formed have limited solubility in water and would therefore have the potential to accumulate during treatment as decomposition may not be instantaneous.
- (3) The decomposition is complex and affected by a number of factors including metals, pH, light and temperature.
- (4) The decomposition of alkyl hypochlorites is autocatalytic.
- (5) The decomposition of the alkyl hypochlorites is strongly exothermic with the potential for a theoretical temperature rise under low heat loss conditions of >1000 K.
- (6) The decomposition will be accompanied by the generation of significant quantities of gas/volatiles.
- (7) Further work would be required in order to define a satisfactory kinetic model for the decomposition of alkyl hypochlorites in a waste treatment scenario.

ACKNOWLEDGEMENTS

Initial raw DSC data files on ethyl hypochlorite and 2 butyl hypochlorite prepared using the method in Appendix 1 with CCl₄ in place of DCM were supplied by J Kay, HSL, Buxton. All analysis on the data was carried out within Syngenta laboratories.

APPENDIX 1: EXPERIMENTAL PROCEDURE FOR PREPARATION OF 1 M BUTYL HYPOCHLORITE IN DCM

(Note a similar method was used for the other alcohols)

Anhydrous dichloromethane (DCM) (40 ml), butanol (3 g) and glacial acetic acid (2.4 ml) were charged to a 100 ml conical flask and cooled to 0°C after 5 minutes this mixture was transferred to a 150 ml RB flask containing 8% bleach (44 ml) at 0°C. (Note: the RB flask and all other connected glassware were covered with black tape to minimise light exposure.) The resultant mixture was stirred for ca. 3 minutes then transferred to a chilled separating funnel.

The lower organic phase was removed and the aqueous phase discarded. The organic phase was washed with chilled 10% NaHCO₃ (3 × 20 ml), then washed with chilled water (10 ml), the organic phase was then dried over anhydrous Na₂SO₄. The solution was then filtered through a No. 50 glass fibre filter paper and the residue washed through with 10 ml of chilled anhydrous DCM.

The resulting Butyl Hypochlorite was charged to a chilled amber glass bottle and stored in the freezer (−16°C) until required.

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