

EXPERIMENTAL STUDY OF THE LIQUID PHASE HYDROLYSIS REACTION OF TITANIUM TETRACHLORIDE[†]

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Titanium tetrachloride (TiCl₄) is used in the chemical industry as an intermediate in the production of titanium metal, catalysts and the pigment titanium dioxide. TiCl₄ is known to react violently with water to release highly corrosive and toxic hydrogen chloride (HCl) gas. However, industry does not have a common and agreed understanding of the assessment of the extent and severity of the consequences of identified possible major accidents such as an accidental spill of TiCl₄. The industry together with the regulatory authorities therefore wishes to make advances on the most appropriate means of estimating the toxic impact from TiCl₄ spillage onto wet ground, using validated assumptions on the reactive chemistry and available computer codes.

However, very little experimental data are available in the literature on the hydrolysis of TiCl₄. Existing spill models are based on theoretical thermodynamic calculations for both the reaction stoichiometry and reaction energy. The objective of the work presented in this paper is to carry out an experimental study of the liquid phase hydrolysis reaction of TiCl₄ in order to verify the input parameters used in the existing spill models.

Hydrolysis reactions were carried out in excess of TiCl₄, since in the case of accidental spills water will most likely be the limited reactant. The experimental investigations showed that the liquid phase hydrolysis reaction of TiCl₄ releases HCl gas and produces a solid material. The quantity of solid produced was measured (for a given quantity of added water) and the solid subsequently chemically analysed. An experimental setup also allowed the measurement of the quantity of HCl gas released during the reaction.

The liquid phase hydrolysis reaction of TiCl₄ was also carried out in both a Dewar calorimeter and in a pseudo-adiabatic calorimeter. These measurements were carried out while varying the water addition rate. The spontaneous, instantaneous and exothermic natures of the reaction were observed and the heat of reaction measured.

These analyses were used to test the reaction scheme published in the literature and to propose an experimentally validated reaction stoichiometry and heat of reaction.

KEYWORDS: titanium tetrachloride, spill, water reactive chemical, calorimetry

INTRODUCTION

Titanium tetrachloride (TiCl₄) is used in the chemical industry as an intermediate in the production of the pigment titanium dioxide, titanium metal and catalysts. TiCl₄ is known to react violently with water to release highly corrosive and toxic HCl gas and some particulate matter. However, industry did not have a common and agreed understanding of the assessment of the extent and severity of the consequences of identified possible major accidents such as an accidental spill of TiCl₄. These types of assessments are needed for emergency planning and the production of site reports required under the Seveso Directives (Seveso, 1996). The industry (represented globally by the Titanium Dioxide Manufacturers Association, TDMA), together with the regulatory authorities therefore wishes to make advances on the most appropriate means of estimating the toxic impact from

TiCl₄ spillage onto wet ground, using validated assumptions on the reactive chemistry and available computer codes.

STAWaRS (Source Term Assessment of Water Reactive Substances) is a code recently developed by ESR Technology (ESR) for the Health and Safety Executive (HSE) which models the spreading and simultaneous evaporation of liquid pools from spillages of water reactive chemicals and accounts for chemical reactions of the spilled material with available water. Further details of this model are available elsewhere in these Hazards XXII proceedings (Cruse, 2011). At the request of the TDMA, and with the permission of the HSE, ESR Technology have also developed a bespoke model for the TDMA for the assessment of spillages of TiCl₄. Both codes are based upon the REACTPOOL model of Kapias and Griffiths (2001), as amended by Tickle (2006) and require data on the physico-chemical properties of the

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spilled materials and their reactions with water. Therefore, HSE and TDMA agreed to collaborate on work to obtain accurate data for the application and validation of the models.

The experimental strategy proposed and agreed for this investigation was to carry out calorimetric analysis of the hydrolysis reaction of TiCl_4 using pseudo-adiabatic reaction calorimeters. These analyses provided some measurements of the heat of reaction in both excess of water and excess of TiCl_4 (representative of accidental spills).

INPUTS USED

The chemistry in the model is based on that proposed by Kapias and Griffiths (2005). They found that the liquid phase hydrolysis reaction of TiCl_4 is not well-established in the literature and after reviewing the available information developed the following exothermic reaction schemes:

- $\text{TiCl}_4(\text{l}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{TiO}_2 \cdot \text{H}_2\text{O} \cdot 3\text{HCl}(\text{s}) + \text{HCl}(\text{g})$
(Reaction 1)
- $\text{TiCl}_4(\text{l}) + 3\text{H}_2\text{O}(\text{v}) \rightarrow \text{TiO}_2 \cdot \text{H}_2\text{O} \cdot 3\text{HCl}(\text{s}) + \text{HCl}(\text{g})$
(Reaction 2)

Table 1 shows the corresponding calculated values of the heat of reaction. This scheme is based on 'theoretical' thermodynamic calculations of the Gibbs free energy and a number of further assumptions namely:

- (a) The chemical type of the solid produced is either $\text{TiO}_2 \cdot n\text{H}_2\text{O} \cdot x\text{HCl}$ or $\text{Ti}(\text{OH})_n\text{Cl}_x$.
- (b) The reaction should evolve one molecule of HCl gas from one molecule of TiCl_4 .
- (c) The hydrolysis reaction is spontaneous ($\Delta G < 0$) and exothermic ($\Delta H < 0$).
- (d) In cases of accidental spills, water will be the limiting reactant with TiCl_4 in excess.

The principal need is to examine experimentally whether the reaction scheme is as proposed by Kapias *et al* and that the above assumptions are appropriate. However, very little experimental data are available in the literature on the hydrolysis of TiCl_4 . The TiCl_4 working group of the TDMA sector group commissioned the Health and Safety Laboratory to carry out the experimental study of the liquid phase hydrolysis reaction of TiCl_4 in

Table 1. Exothermic Heat of reaction proposed by Kapias (2005)

Temperature (K)	ΔH_r Reaction		ΔH_r Reaction	
	1 kJ/mol of TiCl_4	kJ/mol of H_2O	2 kJ/mol of TiCl_4	kJ/mol of H_2O
298	169	56.3	301	100.3
300	170	56.6	302	100.6
400	201	67	333	111

order to test the input parameters assumed and used in the existing spill models. Of particular interest is the heat of reaction for the hydrolysis in scenarios where TiCl_4 is in excess and water the limiting reagent.

EXPERIMENTAL STUDIES: WITH EXCESS WATER

The hydrolysis reaction of TiCl_4 was initially investigated with an excess of water. Two calorimetric tests were carried out using a 500 ml glass Dewar flask as shown in Figure 1. The Dewar was filled with approximately 200g of water and TiCl_4 added at 1 ml/min using a syringe pump (Table 2). The results are also shown in Table 2, with Figure 2 showing the temperature-time curves obtained. The temperature increase is perfectly linear, confirming that the reaction is instantaneous, mass transfer controlled and that the heat losses are negligible compared to the heat generation rate. The power generation is approximately 150 W/kg and the heat losses are approximately 1.5 W/kg (1% of the power generated by the reaction). These experiments also showed good reproducibility. The heat capacity (C_p) of the liquid was assumed to be the C_p of water since water remained in substantial excess throughout the experiment. The heat of reaction was extracted from these results using Equation 1, and was measured to be **295 kJ/mol of TiCl_4** .

$$\phi m C_p \frac{dT}{dt} = \dot{m}_{\text{TiCl}_4} \Delta H_r \quad (1)$$

With \dot{m}_{TiCl_4} the TiCl_4 addition rate in mol/s.

EXPERIMENTAL STUDIES: WITH EXCESS TiCl_4

Calorimetric tests were run in a 500 ml glass Dewar and Phitec II adiabatic calorimeter with TiCl_4 in excess, which is representative of accidental spills. Preliminary experiments investigating this reaction were performed in a glass round bottom flask. Whilst not giving calorimetric results, these additional experiments gave a valuable insight into the reaction being studied.

PRELIMINARY TESTS IN A GLASS ROUND BOTTOM FLASK

Several tests with an excess of TiCl_4 were performed using the glass round bottom flask shown in Figure 3 and Table 3. These tests clearly showed the formation of a yellow solid crust (and not fine particles of solid) as well as the production of gas (HCl) and heat. It was also observed that the thermocouple in the liquid TiCl_4 could become embedded in the solid crust formed, leading to a false reading of the temperature. In order to ensure that accurate temperature readings were obtained, two thermocouples were inserted in the liquid TiCl_4 . Figure 3 describes two of the glass flask experiments that proved important for the design of the Dewar experiment.

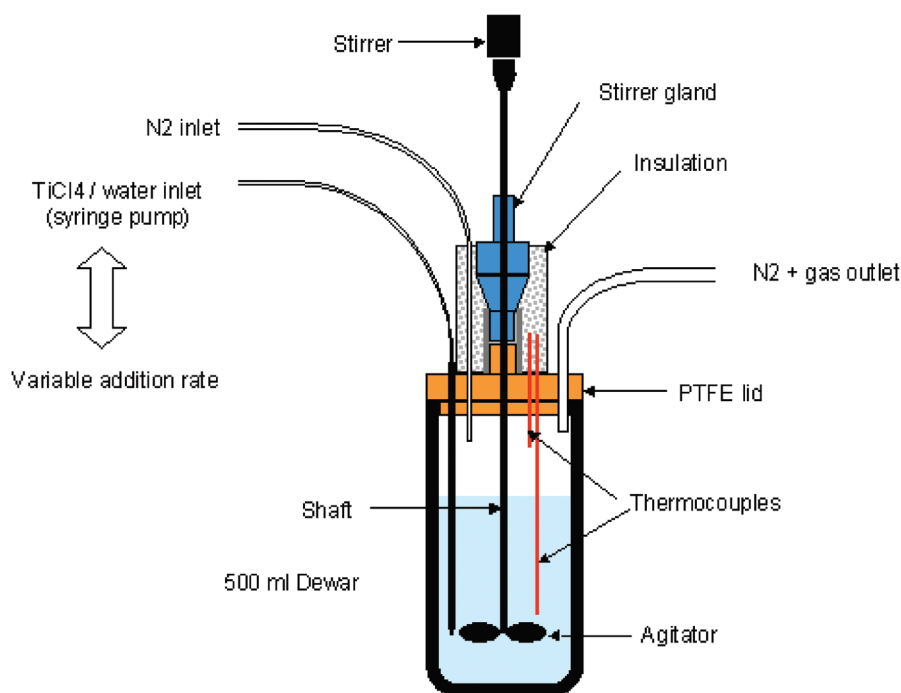


Figure 1. Dewar flask setup

In the first experiment (Figure 3a), water was injected into the liquid TiCl_4 using a syringe pump. For this test, the deep PTFE pipe carrying the water into the TiCl_4 was not touching the blades of the stirrer. The following observations could be made:

- There is a significant accumulation of the solid crust around the water addition pipe. This seems to indicate that as the experiment progresses there may not be good contact between the water and the liquid TiCl_4 , with the solid crust acting as a physical barrier to reaction.
- The solid crust adheres to the glass flask wall surface and is formed as lumps, not as a fine powder dispersed through the liquid.
- Between 1500 and 2500 seconds after the start of the experiment, the two liquid temperature curves are virtually identical. However, after 2500 seconds the temperature readings are different, probably due to the accumulation of the solid crust around the thermocouples. In addition, the observed temperature curve is non-linear, even though the water injection rate remains constant.

These observations indicated that, with this initial experimental design, it was difficult to obtain meaningful temperature curves and subsequently derive the heat of reaction. Therefore, the design of the experimental apparatus was modified.

A second experiment (Figure 3b) was performed with the set-up modified so that the deep PTFE pipe carrying the

water into the TiCl_4 was touching the stirrer blades, such that the blades tapped the end of the pipe as they rotated. Consequently, the solid crust that formed around the pipe was continuously removed and dispersed in the liquid TiCl_4 . As a result, the two temperature curves observed are virtually identical and fairly linear (in accordance with

Table 2. Experiments adding TiCl_4 to an excess of water in glass Dewar flask

	Experiments	
	TiCl_4 flask 04	TiCl_4 flask 05
Initial quantity of H_2O	(g) 201.83	203.23
	(mol) 11.21	11.29
Quantity of added TiCl_4	(g) 12.28	12.34
	(mol) 0.0647	0.065
$\text{TiCl}_4/\text{H}_2\text{O}$ ratio	(w/w) 6%	6%
	(mol/mol) 0.57%	0.57%
TiCl_4 addition rate	(ml/min) 1	1
	(g/min) 1.72	1.72
	(mol/s) 1.52E-04	1.52E-04
ΔT	(K) 15.45	15.63
dT/dt	(K/s) 0.0361	0.0362
ϕ	(–) 1.34	1.34
ΔH	(kJ/mol of TiCl_4) 293	297

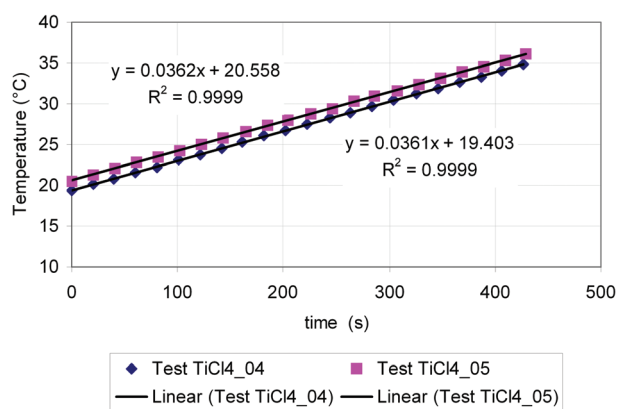


Figure 2. TiCl₄ added to an excess of water in 500ml Dewar flask

the constant water injection rate). The non-linearity (at around 3000 sec) can be attributed to the heat losses of the glass flask and not a false reading from the thermocouples. This improved experimental configuration was used in the subsequent tests undertaken in Dewar flasks.

TESTS IN A DEWAR FLASK

Six tests were carried with two different 500 ml glass Dewar flasks (each possessing slightly different thermal properties) with the set-up in Figure 1, (modified so that the water addition pipe was continually knocked by the stirrer rotor) summarised in Table 4. Figure 4 shows the temperature curves obtained for one of these experiments. The temperature increase is linear (in line with the water injection rate). This indicates that in the presence of an excess of TiCl₄ the hydrolysis reaction is still instantaneous and mass transfer controlled. Heat losses of the Dewar are also negligible compared to the heat generation rate.

The heat of reaction (ΔH_r in J/mol of H₂O) can be extracted from the following thermal balance:

$$\phi m C_p \frac{dT}{dt} = \dot{m}_{H_2O} \Delta H_r \tag{2}$$

With \dot{m}_{H_2O} the water addition rate in mol/s. With TiCl₄ being well in excess, the C_p of the liquid was assumed to be the C_p of TiCl₄ (786 J/kg/K). Thermal inertia factors (ϕ) of the Dewar flasks were measured experimentally. Results obtained from the six tests showed a very good

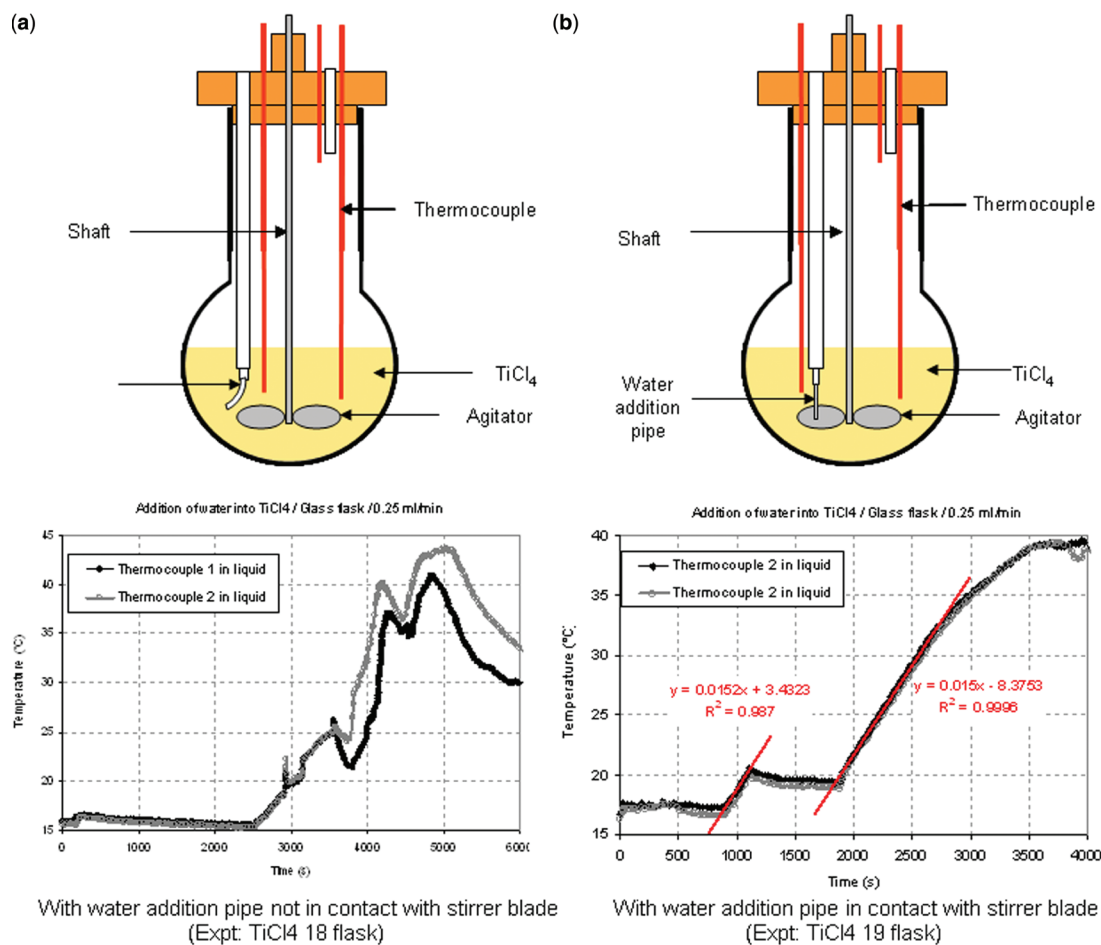


Figure 3. Hydrolysis of TiCl₄, water being the limiting reactant, in a glass round bottom flask

Table 3. Experiments adding water to an excess of TiCl₄ in a glass round bottom flask

		Experiments	
		TiCl ₄ 18 flask	TiCl ₄ 19 flask
Initial quantity of TiCl ₄	(g)	129.7	151.68
	(mol)	0.68	0.8
Quantity of added H ₂ O	(g)	9.5	7.8
	(mol)	0.527	0.433
TiCl ₄ /H ₂ O ratio	(w/w)	13.65	19.44
	(mol/mol)	1.29	1.84
H ₂ O addition rate	ml/min	0.25	0.25
	g/min	0.25	0.25
	mol/s	1.16E-04	1.16E-04

reproducibility. **The heat of reaction, with TiCl₄ in excess, was measured to be 17 kJ/mol of H₂O in the Dewar flask calorimeter.**

ADIABATIC TEST IN PHITEC II CALORIMETER

One calorimetric test was carried out with an HEL Phitec II calorimeter under adiabatic conditions. This gave a linear plot of temperature against time whilst water was added. The corresponding heat of reaction was calculated using Equation 2. Once again, as TiCl₄ was well in excess, the *C_p* of the liquid was assumed to be the *C_p* of TiCl₄ (786 J/kg/K). This was confirmed by the measurement of the *C_p* of the solid + liquid TiCl₄ mixture (829 J/kg/K). **The heat of reaction, with TiCl₄ in excess, was measured to be 13.1 kJ/mol of H₂O in the Phitec II calorimeter.**

This value is less than the value obtained with the Dewar experiments. This may be attributed to the design of the Phitec can; the mixing is achieved by a magnetic stirrer bar and the water addition pipe is a rigid metal pipe which delivers the water several millimetres above this stirrer bar. It is possible that any solid crust may not be removed as it is formed, resulting in non uniform mixing.

ASSESSMENT OF REACTION STOICHIOMETRY

Some of the calorimetric tests described in the previous sections and other specially developed non-calorimetric experimental setups were used to assess the reaction stoichiometry proposed by Kapias (2005) for the hydrolysis reaction with an excess of TiCl₄. The objectives were to:

- Measure the mass of solid produced for a given quantity of added water.
- Make observations on the solid produced.
- Measure the quantity of gas produced for a given quantity of added water.

MEASUREMENT OF THE MASS OF SOLID FORMED

A second experimental setup with a glass round bottom flask was designed to measure the both the quantity of solid produced and the quantity of gas released. The reaction setup, and the protocol followed, is shown in Figure 5, with the results in Table 5.

The dry solid obtained was a fine powder, very different in appearance from the wet solid formed during the initial reaction TiCl₄ + H₂O, which is more like a solid crust. This ‘wet’ solid had about twice the mass of the dry solid eventually obtained; the extra mass being attributed to TiCl₄ entrained in the solid. A glass dish containing the dry solid was left to stand in the fume cupboard and showed a mass gain of approximately 10% in 150 min. Therefore, the solid obtained is either hygroscopic or reacts with atmospheric moisture. The dry solid was also mixed with water whereupon no obvious emission of gas was observed. The solid does not dissolve instantaneously in water but a little mixing is necessary and a fine white precipitate was formed. This hydrolysis or dissolution produced some heat.

The observation of the dry solid would appear to indicate that the more vigorous reaction observed when bringing water and the ‘wet’ solid crust into contact could mainly be attributed to the reaction between the water and the remaining TiCl₄ in the ‘wet’ solid. Measurement of the mass of dry solid gave an average solid/H₂O mass ratio of 4.01, compared to 3.86 predicted by Kapias (2005) in Reaction 2.

Table 4. Hydrolysis of TiCl₄, water being the limiting reactant, in glass Dewar flasks

Dewar flask	Name	Initial quantity of TiCl ₄ (g)	Quantity of added H ₂ O (g)	H ₂ O addition rate		<i>dT/dt</i> (K/s)	ΔT (K)	ϕ (–)	ΔHr kJ/mol of H ₂ O
				(ml/min)	mol/s				
A	TiCl ₄ 20 Dewar	218.48	6.77	0.250	2.31E-04	0.017	25.95	1.39	16.99
A	TiCl ₄ 21 Dewar	209.41	3.42	0.250	2.31E-04	0.017	14.09	1.41	17.17
A	TiCl ₄ 22 Dewar	196.40	3.80	0.250	2.31E-04	0.018	15.60	1.43	16.90
B	TiCl ₄ 23 Dewar	203.96	3.83	0.500	4.63E-04	0.028	13.10	1.71	16.60
B	TiCl ₄ 24 Dewar	215.00	1.77	0.125	1.16E-04	0.007	6.10	1.67	17.36
B	TiCl ₄ 25 Dewar	206.00	3.80	0.250	2.31E-04	0.014	13.20	1.70	17.17

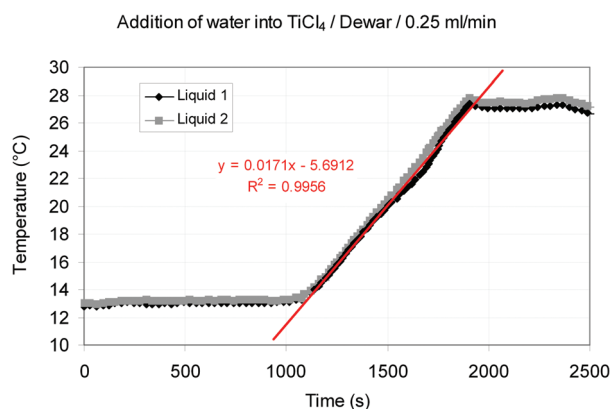


Figure 4. Hydrolysis of TiCl_4 , water being the limiting reactant, in a Dewar flask (TiCl_4 21 Dewar)

PARTIAL CHEMICAL ANALYSIS OF THE SOLID

The dry solid obtained above was analysed in order to obtain the proportion of chlorine within the sample. To do this, the solid was first dissolved in water, followed by a titration of the resulting acid solution using a base (NaOH , 0.1 M, phenolphthalein indicator). A value of 53% (w/w) of chlorine in the solid was measured.

This measurement is consistent with the formula $\text{TiO}_2 \cdot \text{H}_2\text{O} \cdot 3\text{HCl}$ proposed by Kapias (2005), where HCl represents 53% of the mass of the solid. However the structure proposed by Kapias ($\text{TiO}_2 \cdot \text{H}_2\text{O} \cdot 3\text{HCl}$) infers knowledge of the *molecular* formula of the solid (i.e. which atoms are connected to each other). The chlorine content analysed above only supports an *empirical* formula of $\text{TiCl}_3\text{H}_5\text{O}_3$ (i.e. how many of which sort of atom are present). It should be noted that that 53% chlorine content is also consistent with empirical formulae such as TiCl_3O_3 , or TiCl_2O , for example.

A calculated heat of reaction such as that derived by Kapias depends on knowing which chemical bonds are being broken or formed during the reaction. The molecular formulas of the products need to be known (or assumed) for such a calculation to be meaningful.

MEASUREMENT OF THE QUANTITY OF GAS RELEASED UPON HYDROLYSIS WITH AN EXCESS OF TiCl_4

During some of the experiments described above, the quantity of gas released during the hydrolysis reaction was measured by allowing the gas evolved from the reaction to pass through a series of 15% aqueous NaOH traps. The mass gain of these traps is equated to the amount of acidic vapour released. In addition, the amount of gas produced

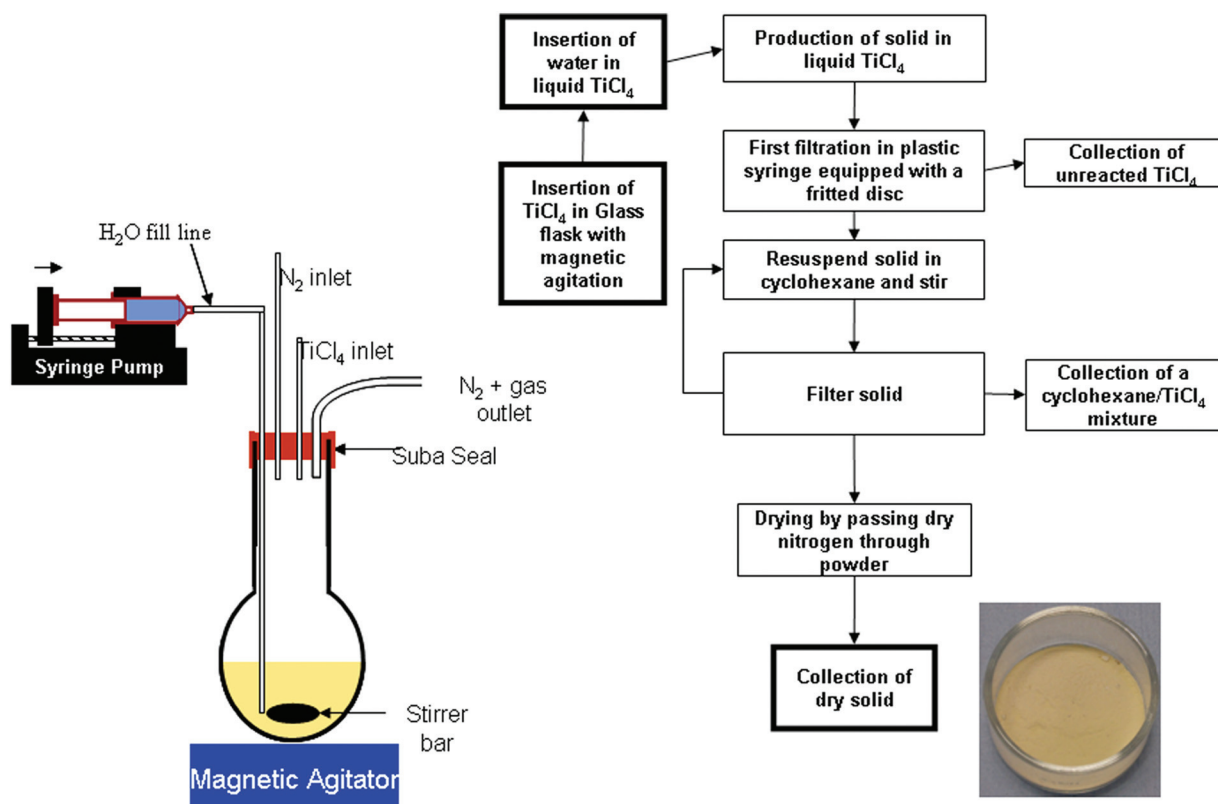


Figure 5. Method of producing dry solid

Table 5. Measurement of the mass of solid produced in excess of TiCl_4

	Initial quantity of TiCl_4		Quantity of H_2O added		Mass of solid (g)	Ratio Solid/ H_2O (w/w)
	mass (g)	n (mol)	mass (g)	n (mol)		
TiCl_4 31	105.72	5.57E-01	0.44	2.43E-02	1.70	3.89
TiCl_4 32	109.83	5.79E-01	0.44	2.43E-02	1.99	4.55
TiCl_4 33	110.00	5.80E-01	0.44	2.43E-02	1.43	3.27
TiCl_4 34	107.00	5.64E-01	0.63	3.47E-02	2.72	4.35

from the Phitec calorimeter experiment was determined from the pressure rise. The amount of gas produced, normalised in relation to the amount of water added to an excess of TiCl_4 , is shown in Figure 6.

It can be seen that these results show a fairly wide variation. Results obtained with the Dewar calorimeter were generally higher than the results from the two other setups. Such variation may be due to some TiCl_4 vapour carried over into the traps (since the end temperature of the reaction vessel was higher) or the formation of other types of volatile titanium species in the vapour phase that can be trapped by the caustic solution.

The result of the Phitec test should be interpreted with the following caveats: the high level of pressure (up to 8 bar) may lead to some acidic gas dissolution in the liquid TiCl_4 . Therefore the measured quantity of gas released may be lowered compared to a situation where hydrolysis reaction takes place under atmospheric pressure, e.g. in an open air spill or in the experimental setup working under atmospheric pressure, developed for this project (Dewar, glass flask, etc). In addition poor mixing of the reagents in the presence of a solid crust may be expected to result in a lower observed value.

These results show that the measurement of the gas released is difficult as the presence of TiCl_4 vapour, the

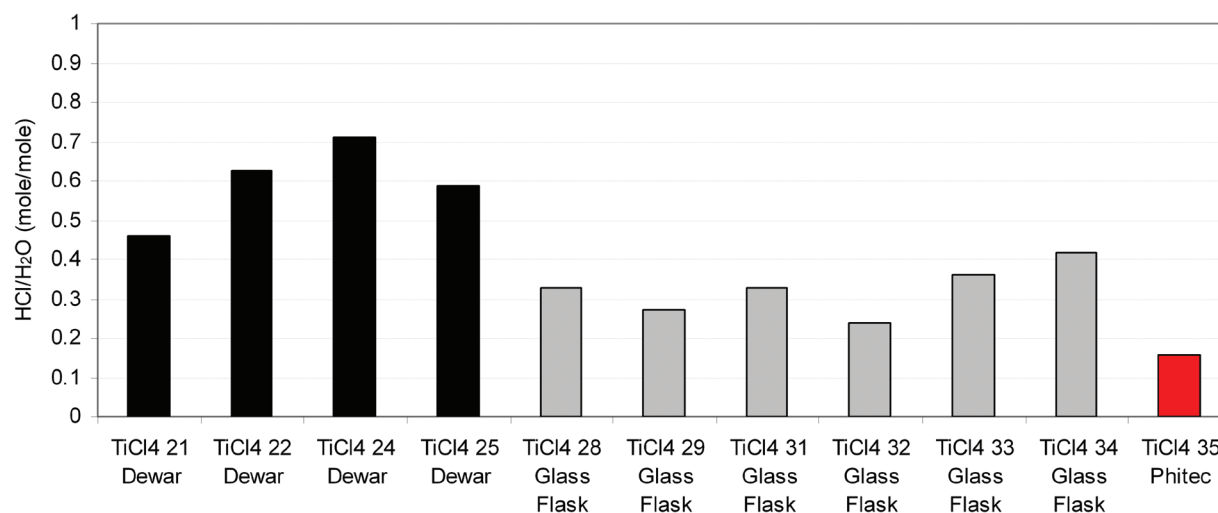
formation of other acidic species and gas dissolution effects can all influence the results.

If the results obtained from reactions in glass flasks with magnetic agitation are believed to be representative of the quantity of gas released (which is also assumed to be pure HCl), by the hydrolysis reaction in excess of TiCl_4 , the average value of the HCl/ H_2O molar ratio is 0.32. Experimental results would then be in accordance with the HCl/ H_2O molar ratio of 0.33 proposed by Kapias (2005) (1 mol of HCl for 3 mol of water). However, there is no firm evidence that experiments performed in glass flasks with magnetic agitation did give representative results. Detailed chemical analysis of the caustic traps at the end of the experiment for titanium content, and a measurement of the solubility of HCl gas in liquid TiCl_4 as a function of the temperature would allow for better interpretation of the results.

CONCLUSIONS

CONCLUSIONS ABOUT THE NATURE OF THE HYDROLYSIS REACTION

A significant part of this work focused on the hydrolysis reaction with an excess of TiCl_4 (representative of spill conditions). Under these conditions, the experimental

**Figure 6.** A summary of the measured amounts of gas released by hydrolysis of TiCl_4 with water as the limiting reagent

work clearly showed the production of a yellow solid crust (and not fine particles of solid) as well as the release of an acidic gas and heat. Formation of this solid crust entrains a significant amount of liquid TiCl_4 . After crushing, washing and drying of this solid crust, a fine yellow powder was obtained, (which was either hygroscopic or able to react with atmospheric moisture).

The dry solid was also mixed with water whereupon no obvious emission of gas was observed. The solid does not dissolve instantaneously in water but a little mixing is necessary and a fine white precipitate was formed. This hydrolysis or dissolution produced some heat.

These observations highlight some of the difficulties in modelling these complex hydrolysis reactions where a variety of solid, liquid and gaseous products may be produced.

CONCLUSIONS ABOUT THE STOICHIOMETRY OF THE HYDROLYSIS

Calorimetric tests and other specially developed non-calorimetric experimental setups were used to assess the reaction stoichiometry proposed by Kapias (2005) for the hydrolysis reaction with an excess of TiCl_4 . Experimental data shows reasonable agreement with the proposed stoichiometry:

- The measurement of the mass of solid produced (solid/ H_2O mass ratio of 4.01) is in agreement with the proposed reaction stoichiometry (solid/ H_2O mass ratio of 3.84).
- The amount of chlorine in the solid (53% w/w) is in agreement with the proposed solid composition ($\text{TiCl}_3\text{H}_5\text{O}_3$, 53% w/w).
- If the results obtained using the glass flask with magnetic agitation were believed to be representative (there is not yet sufficient evidence that they are), the measured $\text{HCl}/\text{H}_2\text{O}$ molar ratio (0.32) would be in agreement with the proposed reaction stoichiometry (0.33). However, it has to be noted that the measurement was performed on the quantity of gas released and not the quantity of gas produced by the reaction, which may differ due to the dissolution of gas in the medium.

However, there is no firm experimental evidence to fully confirm the proposed composition and structure of the solid (if only one type of solid is formed). Some uncertainties also remain regarding the measured quantity of gas released from the surface of the liquid.

CONCLUSIONS ABOUT THE HEAT OF REACTION

The calorimetric tests performed showed that the hydrolysis reaction of TiCl_4 is spontaneous, highly exothermic and mass transfer controlled.

- Reaction with an excess of H_2O : the heat of reaction was measured to be **295 kJ/mol of TiCl_4** .
- Reaction with an excess of TiCl_4 : the heat of reaction was measured to be **17 kJ/mol of H_2O** with a 500 ml Dewar flask and **13.1 kJ/mol of H_2O** with a Phitec II calorimeter. This variance may be due to differences in the design of the two calorimeters; most notably the Dewar flask allowing for a better contact between the liquid reactants. These measured values of heat of reaction are about three times lower than the value 56 kJ/mol of H_2O proposed by Kapias (2005).
- The differences in the values obtained between the cases where TiCl_4 is in excess and where H_2O is in excess could be explained as being due to a different product being formed when TiCl_4 is in excess and water the limiting reagent. It is likely that this product is an intermediate in the complete hydrolysis reaction of TiCl_4 with excess water.

Using these experimentally determined values for heats of reaction within the computer models would most probably result in less conservative outputs for the amount of acidic vapour released, as compared to results obtained using Kapias' proposed values.

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